Radiocarbon dating of iron

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Tiivistelmä Referat – Abstract

Rautaa tuotettiin teolliseen vallankumoukseen saakka pääasiassa puuhiilen avulla. Sulatuksen aikana rautaan sekoittuu hiiltä (0,1-5 %), jonka radiohiilimäärä kertoo prosessissa käytetyn puun elinajasta. Ajoituslaboratoriossa tutkitaan parhaillaan Aikarauta-projektin puitteissa, voitaisiinko Suomessa ruveta ajoittamaan luotettavasti rautanäytteitä ja näin laajentaa ajoitusmahdollisuuksia esihistorian ja historian tutkimuksen avuksi. Ensimmäiset kokeilut arkeologisten rautanäytteiden ajoittamiseksi tehtiin jo 1960-luvulla, mutta vasta 1990-luvulla AMS-tekniikan myötä ajoituksiin tarvittavat näytemäärät saatiin niin pieniksi (0,5-1 mg hiiltä), että testejä kannatti jatkaa.

Tutkimuksen tavoitteena on ollut myös selvittää raudan ajoittamiseen vaikuttavia ongelmatekijöitä (mm. kalkkikiven käyttö juoksutteena, kivihiilen käyttö polttoaineena, puuhiilen oman iän tuoma systemaattinen virhe, raudan uudelleenkäyttö) ja niiden vaikutuksia ajoitustuloksiin. Raudan hiilipitoisuuden ja mahdollisen kalkkikiven käytön selvittämiseksi näytteistä on tehty alkuainemäärityksiä ICP-OES tai ICP-MS-mittauksilla. Tutkimuksessa käytetyt rautanäytteet ovat pääasiassa keskiaikaisia rautanauloja, Virosta saatuja rautaesineiden katkelmia, kiinalaisia rautarahoja sekä rautakuonaa. Vertailunäytteinä on käytetty Rautaruukilta saatua modernia terästä (ei sisällä radiohiiltä), eri juoksutteilla valmistettua omatekoista rautaa sekä kaivauslöytöjen referenssinäytteinä samasta kontekstista löytyneitä viljan jyviä, luita tai hiiltä. Rautanäytteet on esikäsitelty Ajoituslaboratoriossa ja hiili irrotettu ns. CuO-polton avulla, joka on yleisesti käytetty menetelmä radiohiilinäytteiden esikäsittelyssä.

Aikarauta-projektin tutkimushankkeessa on tehty radiohiilimäärityksiä 20 rautanäytteelle. Tulokset osoittavat, että menetelmän käyttö on mahdollista, mutta kontekstin tulisi sisältää myös muuta ajoitettavaa materiaalia, koska monet rautanäytteet antoivat oletettua vanhemman radiohiili-iän. Syynä poikkeamaan saattaa olla sulatusprosessissa juoksutteena käytetty kalkkikivi, koska fossiilinen kalkkikivi laimentaa raudan radiohiilipitoisuutta ja vääristää tuloksia fossiilisten polttoaineiden tavoin. Muita vaihtoehtoja ovat rautanäytteen käsittelyssä käytettyjen työkalujen aiheuttama kontaminaatio tai pajatyöskentelyssä polttoaineena käytetty kivihiili, jonka osuus saattaa etenkin rautanaulojen kohdalla olla syy poikkeaviin ajoitustuloksiin. Raudan uudelleentaonta ja kierrättäminen on ollut yleistä, joten myös raudan oma ikä vaikuttanee tuloksiin. Myös mahdollista turpeen ja kivihiilen käyttöä polttoaineena raudan valmistuksessa tulisi selvittää tarkemmin alkuaineanalyysien avulla. Tutkimuksemme perusteella rautanäytteiden radiohiilimääritys on mahdollista, mutta tulosten tulkinta eli näytteiden varsinainen ajoittaminen on haasteellista.

Avainsanat – Nyckelord – Keywords

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Sisällysluettelo

Cover picture: Iron bloom. All photos: Heidi Nordqvist

Introduction

The dating of iron objects is a challenging task. Even up to the present time it is mostly based on typology. The basic idea of typology is that the objects have become more useful and their manufacture techniques have evolved during the time. Even in ancient times bandwagons had a major influence on the development of different jewellery and ornament styles. With typological analysis of objects an accuracy of 100 years is achieved but utility articles like knives, nails and tools cannot be dated through typology, because these item types have remained similar for centuries and maybe even longer. (e.g. Lavento 2001: 39-41; Lavento 2008: 237-240.) Earlier iron was very valuable material. It was recycled by reforging and even iron nails were re-used. This problematic material forms as well the most typical find material in archaeological excavations of Finnish Iron Age and Middle Ages dwelling sites. The radiocarbon dating of iron can be investigated for pre-industrial iron material, because of the use of charcoal as a fuel for smelting. Charcoal (i.e. wood) carbon was incorporated into metal during the time of manufacture. It contains ^{14}C and its amount reflects the growth time of the used wood. Consequently, this makes attempt to date iron objects worthwhile with the radiocarbon method.

The statistical precision for radiocarbon analysis is ca. 25-35 radiocarbon years corresponding at best to the equal precision in calendar years, which would mean a huge enhancement for the research of Iron Age period in Finland. First attempts to date iron based objects with radiocarbon method were taken already in the 1960´s (van der Merwe & Stuiver 1968), but the research did not continue until the late 1980´s when AMS-technique had become general and the sample amounts needed for the analysis diminished from one kilo of iron to ca. 500 mg of iron powder (Cresswell 1992: 904). The research has proceeded steadily and first attempts to date iron in Finland were made in 2008, when the Finnish Cultural Foundation and the Magnus Ehrnrooth Foundation allocated money for Aikarauta, a research project led by Dating Laboratory. The Aikarauta-project was launched in co-operation with Department of Archaeology and Accelerator Laboratory, University of Helsinki. Project´s main orientation is to scrutiny if it is possible to date iron reliably in Finland and to follow the footsteps of ancient blacksmiths of Finnish folklore and Kalevala. One of our main aims is to find out how the usage of limestone as a flux will take effect to radiocarbon dating results. (Oinonen

et al. 2009.) It is also very important to understand how widely the early iron smelters have used fossil fuels like coke or coal in the manufacturing process or in the blacksmiths forges.

As an opening for the project, a literature analysis (Nordqvist 2008) was assembled. This aimed to survey the methods of the pre-industrial iron smelting processes and the available laboratory analysis to select the processes to extract carbon out of the iron samples on the basis of the quality of the dating results available. Based on the literary analysis, we decided to use the copper oxide (CuO) combustion method in our own research work. This method is commonly known worldwide and it was already in use as the main combustion method for the radiocarbon samples in Dating Laboratory. With iron samples we used sealed double tube combustion method developed by LLNL. (Cook et al. 2001: 221; Hüls et al. 2004.) Because iron samples need higher combustion temperature to extract carbon dioxide out of iron powder, we used quartz tubes instead of glass tubes (Oinonen et al. 2010:177). To avoid contamination we tested our sample-pretreatment procedure first with modern steel reference samples, which should not contain any radiocarbon. With such a mode of operation we could minimize the risks, because the biggest source for contamination comes from the drilling or milling of the sample: without careful preparation and cleansing the drills may contaminate iron with oil or spark of modern steel. The main concern was to avoid adding any modern carbon into sample material: this is why we cleaned all instruments with acetone and milled the iron into powder with aluminium oxide discs (Oinonen et al. 2009:875-880.)

All in all, we investigated 20 different iron samples – world widely over 120 iron artefacts have been dated by using the AMS-technique. The results of this project can now be read from this thesis. Sometimes, it was a difficult task to follow the footsteps of the ancient blacksmiths - their secrets stayed partly unrevealed.

1. THE ARRIVAL OF IRON

The earliest evidence for the use of iron and smelting comes from The Near and Middle East. It is neither possible to trace the accurate locality where iron was first struck nor the precise processing method for early smelting. The technology might have been invented independently in several regions during different periods. The earliest finds are from Mesopotamia, Anatolia, northern Syria, ancient Armenia, northern Iran and Egypt, and these materials are dated back to 5000 BC–3000 BC. Chemical analyses have revealed that some of the artifacts have very high nickel contents, up to 7,5 %, which refers that objects were made of meteoric iron. Pieces of meteoric iron were collected and refined to objects by cold-working, but meteoric iron has played no part in the invention of iron smelting. It is more likely that iron was a by-product of developed copper smelting technology and was found by a chance during the smelting process. (Pleiner 2007: 7, 12-13.) The earliest metal objects date to the 8th millennium B.C. and were made of native copper and malachite (Yener 2000: 1).

The Hittites were the first people who developed a large-scale iron reducing technology in Anatolia, area of modern Turkey, during 1600–1200 BC. Iron trade was controlled by local rulers who consider iron as an extremely precious metal: some of the early iron artifacts were embellished with gold and silver adornments. The secret of iron smelting started to spread in 1200 BC, when the empire of Hittites collapsed. (Huurre 2000: 9; Pleiner 2000: 9.) Iron spread to Palestine during 11th-12th centuries BC and came to Greece and Aegean area through Asia Minor and Cyprus in the 12th century BC. To Persia iron arrived during the 9th-7th centuries BC and spread to India in the 6th-3rd centuries BC. In China cast iron was produced already around 1000 BC. Iron smelting started in Africa ca. 500 BC, but it is still uncertain if the technology was invented there independently or if it came there from the Near East. (Craddock 1995: 234, 261-262; Pleiner 2007: 14-17.)

It took a millennium before iron smelting technology arrived to Europe. Iron came to The Baltic area and Scandinavia through The Balkans, The Carpathian basin and via Bohemia around 1000 BC. (Pleiner 2000: 24.) The real Iron Age and local iron production begins around 500 BC almost simultaneously in Finland, Scandinavia, The Baltic countries, Belorussia and The Northwest Russia (Peets 2003: 13). One reason for

the sudden spread of iron around 500 BC was the war between The Celts and The Romans. The Celts reigned parts of Scandinavia and local iron was a very wanted raw material for weapons. (Holmqvist 1979: 6-8.) In the beginning all iron objects were imported to Finland from elsewhere: there are some early finds whose origins are in the areas of Weichsel, Black Sea and Caucasus. At first most of the artifacts were imported from The Baltic area, but later Scandinavian influences became more important. (Huurre 2000: 9-10.) The oldest iron artifacts from Finland are the two daggers which were found from Savukoski, Northern Finland, in 1961 (Huurre 1983: 298-300). The daggers originate from area of Caucasus and are dated to 500 BC. Iron artefacts with similar age are also iron bracelets, pin and knife from Nakkila (Salo 1981: 267) and some grave goods from Eura Luistari cemetery (Lehtosalo-Hilander 2000: 107-108). Local iron production began during The Pre-roman Iron Age around 300–400 BC (Tiitinen 1990: 11). Remains of early iron furnaces have been found in Northern Finland, Kainuu and Savo. Earliest furnace types were box-like furnaces, where a stone structure was cold-masoned on a pit and dome furnaces. The latter one was a disposable type which had to be broken right after the smelting to get the iron bloom out of the furnace. The early iron smelting continued in Finland till ca. 400 AD, but from the period 500–1000 AD there is only one known iron production site. New artifact types do still emerge and their typological features reveal that items are of local production. Forging and smithery continued, iron slag was still a typical grave offering – but what happened to the iron smelting and where did the iron come from? (Pukkila 2007: 30-31.)

The same phenomenon occurs also in Estonia, Latvia and in The Northwest Russia during 500–1000 AD (Peets 2003: 287-288). At the same time iron production increased in several regions in Sweden simultaneously with the expansion of population and economic growth. During The Viking Age weapon production caused a peak in iron smelting. Viking raids began around the same time and it is supposed that the raids created a base for such an iron trade that local production took a second place. (Stenvik 2003: 124.) After a hiatus of 500 years signs of the iron production emerge again in the archaeological find material at the end of The Iron Age. After this the vernacular iron smelting continued in distant parts of Eastern Finland till the latter part of the 19th century. (Pukkila 2007: 32)

2. THE EARLY SMELTING PROCESS

Various iron smelting processes yield 0-4% contents of carbon inside the iron matrix. If the fuel used in the process has been charcoal, the amount on ^{14}C inside the metal reflects the time of manufacturing the object. Carbon is incorporated into iron during the smelting, when charcoal, ore and flux are mixed together and added into furnace. The most significant factors concerning the radiocarbon dating results are thus the smelting agents like charcoal, coal, peat and fluxes, which may contain calcium carbonates, likewise clay, which has been used in the lining of the furnaces. (Oinonen et al. 2009: 873.)

2.1 The iron ore

The Finnish word for iron, *rauta*, dates from 500 BC and it is of the same root as the Swedish *röd*, red. It refers to the rusty red colour of bog ore, as the Swedish *järn*, originally loaned from the Celtic *izarno,* refers to the dark mined ore and the iron obtained from it. (Turunen 1998: 9.) In Finland iron was usually reduced from lake or bog ore. Ore mining started here quite late if compared to Sweden, where mining activity was carried out already in the prehistoric period. The earliest mines in Finland date back to the 16th century, but they could not produce enough ore. Therefore mined ore and pig iron were shipped from Sweden to the ironworks in the coastal Finland. (Turunen 1998: 11; Serning 1979: 52-53.) In Estonia the iron smelting began 2000 years ago and continued up to the 1350 AD (Peets 2003: 31). Most important iron ores were magnetite (Fe_3O_4), hematite (Fe_2O_3) and limonite ($2Fe_2O_3.3H_2O$ or $Fe_2O_3.2H_2O$). Hematite and magnetite are rocky ores and limonite is lake or bog ore. (Pleiner 2000: 88-89.) Because lake and bog ores were the most important ores in the early iron smelting in Finland, this research will focus on limonite.

Limonite is formed together with hydrogoethite, hydrohematite and hydrolepidocrocite. The name of the mineral comes from the Greek word *leimón,* which can be translated as waterside meadow. (Peets 2003: 31.) Lake ore is formed at the bottom of a lake. Humic acid extracts the iron from loose earth in the form of slightly weathered deposits of gravel and the iron is transported in ground water. When iron-bearing ground water

rises towards the surface and meets organic material, the precipitation of iron oxides is created. Iron usually precipitates on the beds of lakes near the shore. (Sterning 1979: 57-59.) The ore can´t be found deeper than from 3-5 m depth and it usually occurs in places, where trickles and ditches bring iron-rich water from swamp and mire areas. (Lauringson 1995: 53). Limonites usually contain 20–60 % FeO, but the iron content may vary in different parts of the same lake and the chemical composition of the ore also changes through the time. Lake´s floor, topography, depth and size also interact with the formation process. (Pleiner 2000: 88.) The largest deposits of lake ore are found in the moraine and sand based lakes of the Finnish inland regions, which are humous enough to absorb the iron (Kautovaara 1986: 23).In Karelia and Savo area lake ores contain 40-50 % iron (Lauringson 1995: 53). Lake ore is rare in the clay-rich areas and ore does not exist in muddy lakes or in shores where sedge grows. Common types of lake ore are *powder, bean, pea, coin, hail, spool, cake* and *rim ore.* (Rinman 1794: §11; Serning 1979: 57-59.) The ore varies in colour from yellow, brown, brownish yellow and black-blue to greenish (Turunen 1998: 12). Bog ores have been formed equally, but unlike the lake ore, the deposition of bog ore is not continuous. Because of this lake ore is a renewable natural resource. (Kautovaara 1986: 27; Serning 1979: 59.)

Lake ore was lifted with a net, large scoop or a ladle in the summer time to a timber raft, in winter ore was hoisted from holes in the ice. The raft was built of round timber in the spring time, because then the resin rose up to tree´s surface and made the raft as waterproof. Ore was sought in shallow straits and narrows, 1-3 meters deep with a spiked stave. (Lehtinen 1998: 7.) The best time for obtaining bog ore was the early summer time, when the bogs were at their driest. In Norway bogs were even ditched and dried to ease the ore lifting process. Turf layer was peeled off, the ore dug up with hoes and collected in heaps to drain and dry. (Sterning 1979: 59-60.) C. Rinman describes a different method for grassland or pasture areas, where ore was excavated in spring time, right after the snow had melted. The sod layer was removed carefully and set aside and after the ore was dug the hole was carefully recovered with sod. If the ore contained soil, it had to be washed in a screen or on an iron sheet with holes, because the soil would have disturbed the smelting process. After washing ore was piled up and sheltered from the rain. It could be covered by spruce branches or otherwise the ore was stored in a hut. (Rinman 1794: §19.)

After the ore had dried in a pile for a while, it was roasted in a fire at the temperature of 400–800 ºC with free access of air. The roasting resulted in a chemical transformation where non-oxide ores turned into oxides, which was the most appropriate form for smelting. (Pleiner 2000: 107-108.) Roasting also makes ores more porous and thus more amenable to the reduction process, because ore enriches a little and its colour turns dark red (Pukkila 1993: 8). Process also removes organic elements and carbonates from the ore. Because limonite is a hydrated ore, roasting is also needed to remove the crystal water. When hydrated ores are roasted, they lose both free and combined water. For limonite this happens at temperature exceeding 550 ºC and the chemical reaction is as the following: $2Fe_2O_3.3H_2O + \text{heat} \rightarrow 2Fe_3O_3 + 3H_2O$. (Pleiner 2000: 107-108.) After roasting ore was pulverized and mixed with charcoal. Flux, quartz sand, lime or fluor was added into this mixture. (Lehtinen 1998: 8.) At the earliest times ore was not roasted at all, it was just refined in furnace directly from ore to iron (Pukkila 2007: 34).

Picture 1: Pulverized and roasted lake ore for iron smelting.

The introduction of gunpowder and dynamite in the late 19th century undermined the profitability of lake ore, which went out of use in industry because mined ore was easier to obtain and it had better quality. Before the introduction of the puddling method in 1850´s, blast-furnace smelted lake iron lead to surprises, because the phosphorous-rich iron broke from even a small blow when being wrought. (Turunen 1998: 13.) Many rural blacksmiths still used it in the early 20th century, smelting it with traditional methods in their own forges and making tools and implements from it (Ikäheimo 1988: 80).

2.2 The fuel types

Before the 19th century, iron smelting was based on the use of charcoal during the smelting process. There are some exceptions, which are Chinese and Roman iron smelters, who used coal as a fuel very early. Motive for this is in different smelting traditions: the early European smelters produced iron by direct or bloomery process in lower temperatures. The end product of direct process was solid and malleable bloom iron. Chinese produced cast iron by crucible process. The Chinese tradition was based on indirect process: in modern metallurgy indirect process means, that iron is smelted in higher temperatures (1600-2000°C) (Pleiner 2000: 129. 131.) However, they could produce cast iron in very low temperatures (even 1130 °C), because the cast iron has higher carbon content. The Romans used candle coal mostly in smithing operations (van der Merwe 1969: 26.) Even peat has been used in iron smelting (Tylecote 1981: 44).

2.2.1 Charcoal

Charcoal was the most common metallurgical fuel in antiquity. It has a high calorific value, which means it can maintain very high temperatures in a small volume (Craddock 1995: 189). Charcoal produces over 7000 Kcal/kg and if compared to green wood, which calorific value is only 3000 Kcal/kg, it is very effective fuel. Charcoal consists mostly of carbon, which has a high affinity for oxygen and it can reduce the oxides of iron ore with ease. (Pleiner 2000: 116.) Charcoal was usually made of young sprout forest trees, whose age was around 10–25 years. If wood´s own age is as young as this, it does not have a significant effect on radiocarbon dating results. (Oinonen et al

2009: 879.) In Finland alder, birch, spruce and pine were burnt (Lehtinen 1998: 7). Local hard woods were stronger and they also had higher carbon content. After the trees were cut down they were split and left to dry for some months before combustion. (Craddock 1995: 192.) Main problem with charcoal was its high phosphorus content: bark contains even 13 times more phosphorus than trunk and phosphorus would dilute the quality of iron. This is the reason for stripping bark usually off, probably already in the prehistoric times, because it also prevented logs from decaying. According to the tradition trees were usually cut down after midsummer, because then they contained less sap and by the same token less phosphorus. (Bergström 1922: 5, 14.)

Picture 2: Charcoal is ready for iron smelting.

The iron smelting consumed a considerable amount of firewood: the amount of iron required by five swords or ten axes needed all standing timber over an area of 500 square meters (Turunen 1998: 10). Charcoal was burnt in the iron smelting area, because hot charcoal was required during the whole smelting process (Lehtinen 1998:

7). Exception was made in the regions, where iron was produced on a large scale. In these cases ore was delivered to the charcoal burning area – it was a lot easier to transport ore than enormous amounts of timber. (Pleiner 2000: 118.) It took usually place in heaps, piles or pits, but it is not sure which of the methods is the oldest. In Finland and Scandinavia burning occurred in pits. A good site for a charcoal pit was a dry, forested hillock where the humidity of soil did not interfere with the excavation and burning. The pit was several meters deep and was dug in the previous autumn. The logs were piled on the bottom, covered with a half-meter layer of sand or turf. The pit was lit at four openings, which were covered when the logs took fire – the burning was slow and no air admitted, to avoid risk of burning the logs to ashes. (Turunen 1998: 14-15.) Charcoals were burnt slowly and the process lasted about three days (Peets 2003: 37). Best charcoal was prepared from young green wood, which had the sap still in it. The sap keeps the charcoal homogeneous and the humidity generates adequate circumstances for slow combustion. (van der Merwe 1969: 53.) In some parts of Scandinavia the main fuel in the smelting process has also been chopped wood, which was charred in the furnace just before the iron ore was added (Pleiner 2000: 130).

2.2.2 Coal and peat

The other fuel types were only rarely used in the early iron smelting. From the Roman period there is some evidence of the use of mineral coal in some sites in Britain and the Rhine provinces. It seems that coal was mixed into charcoal during this period. Coal was not usually used for smelting, because it increased the sulphur content of iron and affected metal´s quality. Main reason for the early use of the coal was that blacksmiths used it for working iron. China is an exception: the local metallurgical tradition was based on an indirect method and because Chinese mineral coals have very low sulphur content, the iron smelting was based on the use of coal as early as since the Han period (206 BC-220 AD). The Chinese iron smelters also used special briquettes, which were made of coal-dust, quartz and clay. (Pleiner 2000: 129-130.) It also seems that Chinese iron smelters used coal only in a crucible process (van der Merve 1969: 54). Still, in the antiquity and the Middle Ages coal was mainly used only in blacksmith's forges

The systematic use of coal in Europe started in England in the beginning of the 18th century: in 1709 coke was used first time in England to produce cast iron. The use of

coke was adopted in France at 1759, in Ruhr at 1850´s and in USA´s Pennsylvania it was first used in the 1830´s, but the Swedish industry used charcoal until into the 20th century. (van der Merwe 1969: 54-55.) It is supposed that in early metallurgy signs of coal or coke usage may refer into cast iron technology. Coal-smelted iron can be identified through elemental analysis - it has substantially higher sulphur content than charcoal-smelted iron. (Craddock 1995: 196-198; van der Merwe 1969: 30.) Many evidences show that coke has been an important fuel in the blacksmiths forges already in The Iron Age. Comparing to coal, coke may have been used because the undesirable features of coal can be eliminated through a simple process, where coke is formed from coal. The formation process is quite similar to charcoal making. Coke has a much higher heating value than charcoal and it can give rise to higher furnace temperatures – this is probably a reason why blacksmiths preferred coke instead of charcoal or coal in their forges. (Park et al. 2008: 2469.)

There is also evidence of using peat charcoal as a fuel in prehistoric and early medieval Scotland and Ireland (Tylecote 1981: 44). Peat was dried into blocks and charred, and later converted into charcoal. Peat´s own age can be thousands of years, so it will have an effect to the radiocarbon dating results. (Pleiner 2000: 129.) Some of our iron samples from Estonia have signs of a possible use of peat during the smelting process, but the analyses are still unfinished and it is unclear if the iron is produced in Estonia or possibly in Norway (Jüri Peets, PhD, personal communication). Charcoal and peat remained as the main fuels till the 17th-18th centuries, because other fuels could not generate as high temperatures as the smelting process required (Peets 2003: 37).

2.3 The flux types

Limestone ($CaCO_3$) and other carbonate rocks are usually mentioned as the main fluxes in iron smelting. Flux has been added as a slag former. In early fining processes lime played a role in moderating the influence of high phosphorus contents. The flux has been used to lower the melting point of slag and at the same time iron ore also reduces in lower temperature. The primary purpose of flux is nevertheless to replace iron oxides in the slag and release more iron from the ore (van der Merwe 1969: 30). The role of

lime flux in early smelting process might have been exaggerated – the lime or silica flux acts principally in the range of 1300–1400 °C and such temperatures were not possible to reach with primitive furnace types. If lime has been used already in the early times, pieces of lime should have been pulverized, because flux cannot be absorbed by slag if temperature stays below 1200 °C. (Pleiner 2000: 136-137; Tylecote 1987: 329-330)

The earliest signs of the use of lime are from Württemberg in South Germany and this site dates back to the 7^{th} – 8^{th} centuries AD (Pleiner 2001: 51). Limestone was the most usual flux in the blast furnace process, where its use can be taken for granted. Mass production and the development of blast furnaces were the reasons why the use of lime became more common during The Middle Ages in Europe. (Cresswell 1992: 902). It is presumed, that the use of lime came on in Finland in the 17^{th} century. Before that the Finnish iron smelters used bone as a flux. (Lehtinen 2000:8.) The Scandinavian and Finnish blast furnace iron have had considerable contents of calcium (Ca) and magnesium (Mg), which indicate the use of limestone and dolomite as a flux. The content of $CaCO_3$ in bloomery slag is usually 3-6 %, higher content than that is quite exceptional and may result from local interaction between the slag and calciferous furnace lining rather than from intentional addition of limestone as a flux. (Pleiner 2000: 136-137.)

In some cases in Russia there are pottery finds with pieces of slag – it is thought that these vessels were crucibles and were used to carburize iron while producing steel, when quartz sand and salt were used as a flux (Peets 2003: 49.) Quartz sand was widely used – in Finland it probably had more important role in smelting process than lime flux. Sand has also been used to remove hammerscale during forging by melting to fayalitic slag. Organic materials like urine is used for tempering iron, but this doesn´t have a significant effect to dating results. Old slag may have used as a flux by mixing it together with sand and soil. (Pleiner 2000: 255,288.) Bone, antler and shell have been used as well. Bone-charcoal is used to carbonize bloomery iron. In Scandinavian mythology there are references of using human bones as well. (Gansum 2004: 42; 44.) If organic flux like bone is used and the carbon it contains is nearly contemporary with the charcoal, this extra carbon does not affect significantly on the radiocarbon dating results.

2.4 The smelting process

Iron metallurgy is usually divided into two traditions, the direct and the indirect process. In the direct process iron is reduced directly from ore to bloomery iron. Steel is produced by adding carbon to bloomery iron – the process is known as cementation. The direct process was in use in the West before the 1380´s. However, in China iron was reduced into cast iron - this technique is called the indirect process. Cast iron was refined into steel and wrought iron through decarburization. The indirect process spread to Europe in the late 14th century and these two traditions were the base for modern iron metallurgy and iron industry. In the direct process smelters used much lower temperatures compared to the indirect process, except the Chinese cast iron smelters, who could reduce iron´s smelting point because of cast iron´s high carbon content. (van der Merwe 1969: 8-9, 26.)

The prehistorical iron smelting sites can be identified from the environment with slag heaps and charcoal kilns. The furnaces are not usually preserved, because they were often broken after the smelting process. (Huurre 2000: 10-11.) Magnetometer survey is also an applicable method to prospect for iron smelting sites. Slag is the most typical archeological find material. (Stenvik 2003:127.) Sometimes there are also pieces of ceramics which have remains of iron slag (Huurre 2000: 11). The earliest furnace types in Finland were rectangular and simple, they were dug into the soil and piled up three or four flat stones, base and roof stones. These furnaces were box-like, they had bellows on an open side and ore and charcoal were piled into furnace in layers. (Lavento 1996: 72-73; Lehtinen 1998: 5.) Box-like furnaces were typical in East Carelia (i.e. Karelian Republic), Finland and Norway. It seems that this type of furnace was already in use before The Common Era till The Middle Ages. Second typical furnace type is the dome furnace. Furnaces were masoned of clay and stones, usually partly underground. This type was in use at the latest in The Pre-Roman period. It is not clear if the dome furnaces were coeval with box-like furnaces, or had this type been in use just to remove the impurities from the iron. (Huurre 2000: 10-11.) Third prehistorical furnace type was the bloomery furnace. It was made by digging a stone-lined pit-shaped furnace about a meter high into sloping sandy soil. (Turunen 1998: 10.)

Picture 3: A modern version of ancient smelting process: the tube is a tuyere, which blows air into the furnace. Slag is flowing out from the tapping hole.

The whole smelting process took place in quite a small area, usually near the source of ore. Ore was roasted and charcoal burnt next to the iron furnaces. The furnaces are usually difficult to perceive or already destroyed, but smelting sites can be localized by slag heaps or slag pits and charcoal kilns. The furnace was loaded from the top by charcoal and ore and the air was directed into the furnace via tuyeres with bellows. Iron was reduced in 1200-1350 ºC temperature and lump of iron was formed at the bottom of the furnace (Peets 2003: 44). The slag was removed through a temporarily closed opening at the lower side of the furnace. It has been estimated that 300-500 g of iron was received per one kilo of iron slag. (Huurre 2000: 11.)

Picture 4: The traditional vernacular furnaces were broken after smelting. Blacksmith Seppo Kallio in action.

The invention of blast furnaces during 1100–1200 AD created a basis for more intensive production of iron. The furnace originated in Sweden where it was used to make pig iron. Blast furnaces developed from archaic shaft furnaces, but in distinction these were reusable and did not need to be lined with clay after every instance of use. (Turunen 1998: 15-16.) With blast furnaces it was possible to reach higher temperatures (1300-1400 ºC) and the use of limestone as a flux became more general at that time (Craddock 1995:250). In the backwoods of Finland the vernacular bloomery furnaces were in use and heated up with charcoal as late as the 1850´s. The proper and more effective blast furnaces came to Scandinavia at the beginning of the 17th century. At the same time coal gained ground in Europe as a fuel which causes complications in radiocarbon dating results. The fire chamber of the furnace was filled from above with a mixture of crushed

ore, limestone and charcoal. The golden age of Finnish industrial blast furnaces was in the late 19th century, when furnaces could operate without interruption for years. The on-going smelting process could last over one year. (Turunen 1998:16.)

3. THE RADIOCARBON METHOD

3.1 The basics of radiocarbon dating

Radiocarbon measurements are used in archaeology, cultural heritage, geology, biological sciences, radiation protection, aerosol science and environmental studies (Palonen 2008: 10). The ^{14}C method is a dating technique, which is based on the use of natural radionuclides functioning as chronometers. Radiocarbon method was developed by W.F. Libby (Arnold & Libby 1951: 111-120), who bestowed the Nobel Prize for Chemistry upon his work for age determinations in several branches of science (Taylor 1987: ix). Radiocarbon dating was a revolution for archaeological research in the 1950s, because now sites could be dated by archaeologically significant materials like wood, bone, antler, seeds, charcoal, shell and textiles. Later it was established that radiocarbon ages should be corrected for systematic changes in radiocarbon production rates. (e.g. Tuniz et al. 1998: 227-228.) In 1977 the first radiocarbon samples were dated with the accelerator mass spectrometry-technique (AMS) in the USA. During the 1980s AMS technique became a major contributor to the prehistorical and historical studies and a major feature of this application is the use of small sample size. (Andersen 2007: 91.) Worldwide more than 50 laboratories have developed or are now using AMS capabilities and now the trend in instrumentation is to move to smaller accelerators (Palonen 2008: 10). The most famous AMS results in archaeology are the dating of the Turin Shroud, the Ice Man and the Dead Sea Scrolls (e.g. Tuniz et al. 1998: 228).

The radiocarbon dating method is an isotopic technique, which is based on radiocarbon (^{14}C) and it covers time periods from a few hundred years ago to as far as 50 000 years back. ^{14}C is a radioactive carbon, which occurs naturally and is continually formed in the upper atmosphere continuously by the interaction of neutrons produced by cosmic rays with nitrogen atoms (Bowman 1995: 10). Plants and animals absorb radiocarbon via photosynthesis and food intake. When a living organism dies, no new carbon is added anymore and the amount of radiocarbon starts to decay according to its half-life. (Cook et al. 2003b: 15, 21.) Radiocarbon decays by emitting a beta particle to form ^{14}N and a neutrino. The half-life of ^{14}C is 5730 years and year A.D. 1950 is used as a zero

point from which the scientists count the ^{14}C time. The conventional radiocarbon dating is based on detecting of the ^{14}C decay products whereas the AMS technique measures the amount of radiocarbon directly to determine the age. Though the principles of conventional and AMS- techniques are quite different, the results can be interpreted in similar ways. (Bowman 1995: 31; Taylor 1987: 4.) ^{14}C determinations are accompanied by an expression of analytical or experimental uncertainty (±). The radiocarbon age estimates are usually expressed in years B.P., which means years before the present aka 1950 AD. (Stuiver & Polach 1977: 355-363; Taylor 1987: 5.) The rate of natural ^{14}C production fluctuates with regard to geographical locality. The amount of ^{14}C produced is a function of neutron intensity and the cosmic-ray neutron intensity is about five times higher in the geomagnetic poles than at the magnetic equator. This phenomenon is known as a latitude or altitude effect and it has been reported in tree rings of similar age growing at different locations and it may cause an age effect of about 40 years. A radiocarbon measurement is always accompanied with a measurement of a ratio of ^{13}C to ^{12}C i.e. $\delta^{13}C$ value. (Taylor 1987: 7-8, 34-35.) It may provide information on ingredients used in iron manufacturing.

3.2 The calibration and errors in radiocarbon results

A radiocarbon year is not a true unit of time, but it is variable in length. Conventional radiocarbon ages are given in years before present (BP), where present is 1950 AD. BP-years are calculated using the Libby´s half-life (5568 yr) and the assumption that the production of radiocarbon has been constant. Libby´s half-life is known to be 3% too small and it causes difference between the dating results of the Holocene tree-ring samples, which are measured by radiocarbon method and dendrochronology. The difference derives also from secular variations of the radiocarbon production rate in the atmosphere, caused by the geo- and heliomagnetic effects and variations in the parameters of the carbon cycle. Between 0 and 200 yr BP there have been additional changes in the atmospheric ^{14}C concentration due to industrialization and it causes difficulties in dating this period. (Tuniz et al. 1998: 230.) There are many different calibration curves to use to convert radiocarbon years into calendar years, but sometimes archaeologists prefer working in uncalibrated results rather than calibrate

them. Unfortunately radiocarbon timescale can be used as a relative dating technique only in a rather limited sense. There are several periods in the calibration curve where events which are separated in calendar time by several centuries appear contemporaneous from their radiocarbon results. The most difficult period is the British Pre-roman Iron Age (c. 800-400 BC). (Bowman 1995: 57.) The most popular and probably also the easiest way to calibrate radiocarbon data is to use the OxCal program, developed by Oxford Radiocarbon Acceletor Unit. The current version is 4.1 and it is free to use it online. (Oxford Radiocarbon Acceletor Unit 2011).

There are also three major reservoir effects that may cause local differences in radiocarbon results. These are *marine, hard water* and *volcanic effects*. Marine carbonates and remains of marine mammals such as seals and whales cannot be dated accurately; the marine effect may cause an error of several centuries and is caused by fossil carbon reservoirs and slow cycling of old carbon within oceans. (Bowman 1995: 24-27.) Within the Baltic Sea, due to a complex history of a basin, the effect is somewhat changing both spatially and temporally and this subject requires additional research (see e.g. Oinonen et al. 2010). The somewhat related hard-water effect refers to carbonate-rich areas with the presence of calcium ions resulting from dissolution of the infinite-age calcium carbonate. Calcium carbonate causes similar difficulties to the dating results as the marine effect, but does that also in freshwater areas. The volcanic effect results from volcanic gases including carbon dioxide. This carbon has no ^{14}C activity and it dilutes the local ^{14}C concentration. The volcanic effect causes problems only in volcanic areas. Smaller errors in radiocarbon data are caused by the *northern-to-southern hemisphere* and *the island effects*. In the southern hemisphere the radiocarbon results are systemically 30 radiocarbon years older than in northern hemisphere. This effect is believed to be caused by the greater ocean surface area in the southern hemisphere. The island effect occurs as well from the increased water masses around the islands. (Bowman 1995: 24-27.)

There are several factors making it really difficult to date materials of the last 400 years. Beginning about A.D. 1650, natural ^{14}C variations created a situation in which it is not possible to assign an actual calendar age to any sample derived from this time period to better than about a 300-year time span unless “wiggle-matching” corrections are employed. ^{14}C concentrations were seriously affected by human activities during the

19th and 20th centuries. The industrial effect (aka Suess effect) was caused by the combustion of fossil fuels and atomic bomb effect (or nuclear effect) as a result of the nuclear tests in the post-World War II period. Because of their great geological age, coal, oil and natural gas contain no measurable amounts on radiocarbon. Combustion of fossil fuels dilutes the ^{14}C concentrations, because it adds to the atmosphere CO_2 that contains no radiocarbon. As a consequence of the testing of nuclear weapons, between 1955 and 1963 the ^{14}C activity in terrestrial organics almost doubled. Combustion of fossil fuels may have compensated for the increase of artificial ^{14}C in the atmosphere, but still, combination of these effects may cause that a ^{14}C age estimate is reported as modern. (Taylor 1987: 35-38, 97.)

4. THE DATING OF IRON AND IRON SLAG

Various qualities of iron contain 0-5 % of carbon. Assuming that the iron has been produced by using charcoal as fuel, it may be suitable for radiocarbon dating. Iron has usually been reduced with young wood (approximately 10-25 years old) whereupon the ^{14}C age of carbon, which implies the date of cutting the tree is almost contemporary with the smelting process in archaeological scale. Dating results should be reliable, if the iron smelters have used only contemporaneous charcoal – old wood, coal, peat and geological carbonates like limestone and siderite may cause an age error even of thousands of years. (van der Merwe 1969: 5-6.) The radiocarbon method is not suitable dating method for modern steel made after 1800 AD or for materials that are reheated or re-forged using coal or its composites (Cook et al. 2003b: 22). Recent iron production in blast furnaces utilizes coke, coal and oil, which are all ^{14}C-free (Nakamura et al. 1995: 629).

4.1 The research history of the radiocarbon dating of iron

The idea of dating iron with ^{14}C-method was first invented by Karl K. Turekian. He considered the role of geochemistry in archaeology and believed that ^{14}C-technique could distinguish non-radiogenic fuels like coal from radiogenic, which might indicate the date of manufacture of an artifact. Nikolaas van der Merwe is still the pioneer in dating of iron for conventional radiocarbon dating. Van der Merwe and Minze Stuiver started their work at the 1961 with *beta counting*. (van der Merwe 1969: 3-4.) They demonstrated that it is possible to extract carbon from iron and date it by radiocarbon method. They dated 15 samples, but beta counter required significant amounts of carbon. If the carbon content of iron was 0,1 %, the sample size needed was 1000 g – this was absolutely too large amount to date irreplaceable archaeological artifacts. (Cook et al. 2003b: 16.) The samples were separated into three different categories: (1) the preconditioning/contamination trials, (2) the samples of known age and (3) the materials from the period, when iron industry was starting to use a mixture of coal and charcoal in smelting process (Cook et al. 2003a: 95-96). Van der Merwe also started a

new project to date iron at Pretoria in the late 1970´s, but because of poor accuracy the work was discontinued. (van der Merwe & Stuiver 1968: 48-63.)

In the early 1980´s Edward Sayre et al. repeated two of van der Merwes measurements and analysed samples of the pre-Elizabethan iron bloom. They used small counters, but sample sizes were still tens of grams. Though AMS studies were suggested to Sayre (Sayre et al. 1982: 441-451), method was not tested for iron samples until in the 1987, when Richard Cresswell and his research group developed new methods for *AMS-technique* and dated 12 different iron artifacts (Cresswell 1992: 898). New dating method required only 3.4 g to 274 mg of iron powder per sample and now the wider range of iron sample types were feasible to date, especially when the required amount of carbon diminished into 1 mg. Earlier it was difficult to get dateable materials, because museums and collectors were not willing to sacrifice their artifacts. (Cook et al. 2003b: 16.) At 1990´s, Japanese researchers developed different methods for carbon extraction and dated several ancient iron samples (Nakamura et al. 1995: 629-636; Igaki et al. 1994: 4-8; Oda et al. 1998: 561-564).

In 2001 Andrea Cook and his research group introduced a new carbon extraction method, *CuO-combustion*. The method is discussed more widely in chapter 5.2.2. Compared to earlier techniques CuO-combustion was greatly simplified procedure. Cook and his group re-dated nine of the same samples which van der Merwe had dated in the 1960´s and they compared the results from beta counting versus AMS and flow-through versus sealed-tube extraction methods. (Cook et al. 2003a: 96.) They also tested the dating of different corrosion products, which had rusted in the air, in the ground and in underwater conditions. Plausible dating results were achieved even from completely rusted samples. (Cook et al. 2003b: 16-17.) Matias Hüls and his group followed Cook´s method and tested its accuracy and carbon extraction efficiency with modern iron and archaeological iron samples (Hüls et al. 2004: 710-711). Andreas Scharf´s group had noticed that low carbon content made the sample sizes too large for some of the combustion systems and they tried to find new ways to extract carbon from the samples. They tested *direct sputtering* of the unprocessed sample and *chemical extraction* of carbon, where the carbonaceous residue was dated. (Scharf et al. 2004: 175.) Latest research has been done in Korea considering pretreatment and carbon extraction methods (Park, J. et al. 2010: 1295-1300; Park, J.S. et al. 2010: 1312-1321) and in

Germany, where Hüls et al. have familiarized with the possible risks of contamination which might come from the tools, which have been used during the pretreatment of iron samples (Hüls et al 2011: 151-160).

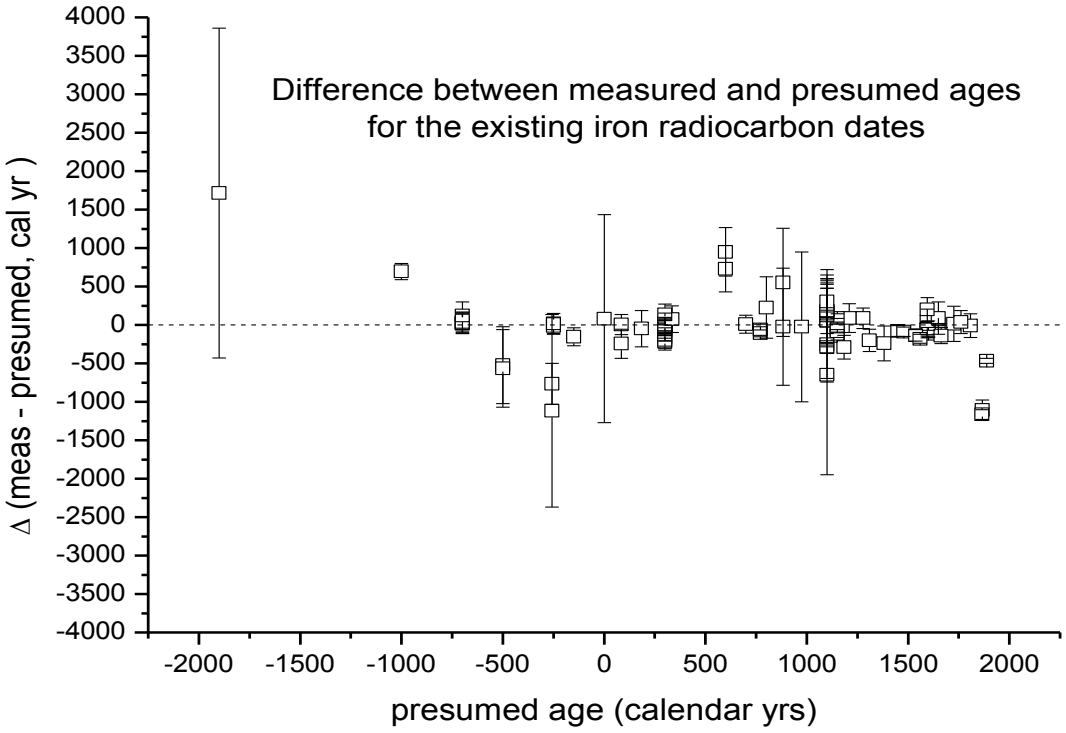


Figure I: 114 iron samples have been dated by ^{14}C-technique thus far.

So far over 120 iron-based items have been dated by the AMS-method (see: Fig I above and Table I in appendix). The determined ages range from The Modern to ones approaching the era of the beginning of The Iron Age (4000-5000 BP). Sample´s carbon contents have ranged from 0,01 % to 3,92 % and sample conditions varied from clean metal to very corroded and rusty iron. It seems that rust is not a barrier for dating – more important is that iron is manufactured using only contemporaneous charcoal. As mentioned earlier, dating results are skewed if limestone, old wood, coal, peat or re-working has been used. In short, iron artifact cannot be dated if it is manufactured or re-heated using coal or if it is made of composite material. (Cook et al. 2003b: 21-22.) The

carbon content should preferably be over 0,5 %, otherwise the sample size will be too large. The museum pieces are usually chemically treated to prevent corrosion and cannot be dated without careful cleaning with toluene, acetone or alcohol. (Scharf et al. 2004: 176.) When choosing the cleaning chemical, it is good to bear in mind that it may contain additional carbon which could contaminate the sample.

5. THE IRON SAMPLE PRETREATMENT PROCESSES FOR ^{14}C ANALYSES

5.1. The sample pretreatment

Rust is a challenge for radiocarbon method. Old artifacts are usually heavily oxidized and it is difficult to find clean metal for samples without damaging the valuable archaeological artifacts. Earlier rust was removed from iron samples in the fear of adding the risk of contamination. Van der Merwe considered possible that rust adsorbed CO_2 from the atmosphere and possibly contained occluded organic materials. He tried to remove adsorbed carbon dioxide by dry peening and washing the sample in acetic acid (CH_3COOH). (van der Merwe 1969: 70.) Richard Cresswell was concerned that corrosion, ground waters, dust and sample storage in carbon based fluids can have influence on dating results. He pretreated and cleaned his samples using abrasion, cold ultrasonic bath in 10 % nitric acid (HNO_3), de-ionized water, methanol (CH_3OH) and finally baking the samples in the temperature of 80 °C overnight. (Cresswell 1992: 89.) Andrea Cook has adapted Cresswell´s method, but no pre-cleaning with nitric acid was undertaken in her research. The samples were cut with a diamond saw. (Cook et al. 2003a: 96, 99.)

Hiroki Enami and his research group cut samples from artifacts by using a metal cutting tool with a whetstone blade. The samples were pre-treated with 1,2N NaOH solution for 1 hour to eliminate organic contaminents and humic acid. After that the samples were treated with 1,2N HCl solution at 60 °C for 5-10 minutes to eliminate carbonate. In the end the samples were rinsed with distilled water and dried. (Enami et al. 2004: 221-222; Igaki et al. 1994: 6.) Hüls and his research group cleaned the samples mechanically from rust until bright metal was exposed. The iron samples were reduced into small pieces by drilling and milling and fatty coatings were cleaned off with acetone (CH_3COCH_3). (Hüls et al. 2004: 710.) Normally the samples are abscised with milling cutter, which may increase the risk of abrasion and contamination. Unlike steel tools used for cutting, archaeological iron artifacts have usually very low carbon content. That is why even a small amount of abrasion from the modern cutting tool may affect on dating results considerably. (Scharf et al. 2004: 175,179-180.) If cutting oil is used for drilling, it must be removed with acetone to avoid contamination (Cheoun et al. 2004: 218). Scharf criticized the cutting and milling of the iron and preferred that the

samples should go through the preparation process as a whole, if possible. Machining should be reduced to the minimum and the samples must be cleaned carefully afterwards. (Scharf et al. 2004: 175,179-180.)

The contaminantion may occur on a site where the sample has been taken. It depends on the type of the contaminant to choose the type of special pretreatment procedures are needed. The contaminants can be carbon-containing materials which may change the radiocarbon age of the sample, or other chemicals like sulphur compounds. The latter causes difficulties in sample processing and it may be hard to produce a pure derivate from the carbon. Many of the preserving and conserving materials contain carbon that may be impossible to remove. Such materials are for example glues, biocides, polyethylene glycol (PEG) and polyvinylacetate (PVA). Also packing materials contain carbon and are potential contaminants. These are paper, cardboard, cotton wool and string. (Bowman 1995: 55-56.)

5.1.2 Corrosion and rust

The corrosion of iron activates when environmental relative humidity (RH) exceeds 20 % and chlorine compounds and oxygen are present. When an artefact is unearthed in excavations its surrounding environment alters quickly and the corrosion process accelerates. Rust is composed of corrosion products, iron salts and other iron compounds, of which colour fluctuates from light yellow to dark brown. Most of the iron salts are water-soluble and soak into the soil and stain it. First corrosion products are ferric chloride ($FeCl_3$) and iron hydroxide [($Fe(OH)_2$) or ($Fe(OH)_3$)]. Blueish black colour on artefacts surface is iron oxide (Fe_3O_4), and it protects iron against corrosion. The corrosion of iron begins from the surface, but by reason of the working technique of iron the crystal structure of metal is not homogenic but bedded. That is why corrosion proceeds along the lines and folds in metals structure. Because the volume of corrosion products is bigger than iron´s, artefacts are usually warped and original surface cannot be seen in the field. (Tomanterä 2008: 6-7.)

Later there has been a lot of discussion about the dating of the rust. Successful experiments have been made already in the 1960´s by van der Merwe and in 2001 Cook

and his group managed to yield reliable radiocarbon dates from rusty samples. Most of the carbon in iron is in the form of iron carbide (Fe3C), also known as cementite. Microstructural analyses have shown that iron carbides remain also in rust. If rust has remains of the original carbon left, the sample can be dated by radiocarbon method. If rust can be dated, the samples can be taken with minimal material and minimal risk to the artifacts. According to Cook, it seems that iron artifact that had been cleaned and then left to rust will give similar dating results as those from clean metal samples. (Cook et al. 2003a: 100; Cook et al. 2003b: 17.) Archaeological museum pieces are quite often contaminated, because during the restoration process iron artifacts are usually chemically treated to inhibit corrosion. Contaminants can be removed with de-ionized water, methanol (CH_3OH), acetone or tetrahydrofuran $(CH_2)_4O$). Scharf and his group tested the Soxhlet extraction process – they used solvents which consisted of tetrahydrofuran, trichlormethane ($CHCl_3$), acetone, methanol and de-ionized water (Scharf et al. 2004: 176). To get reliable dating results, iron samples should be taken before any restoration processes are conducted.

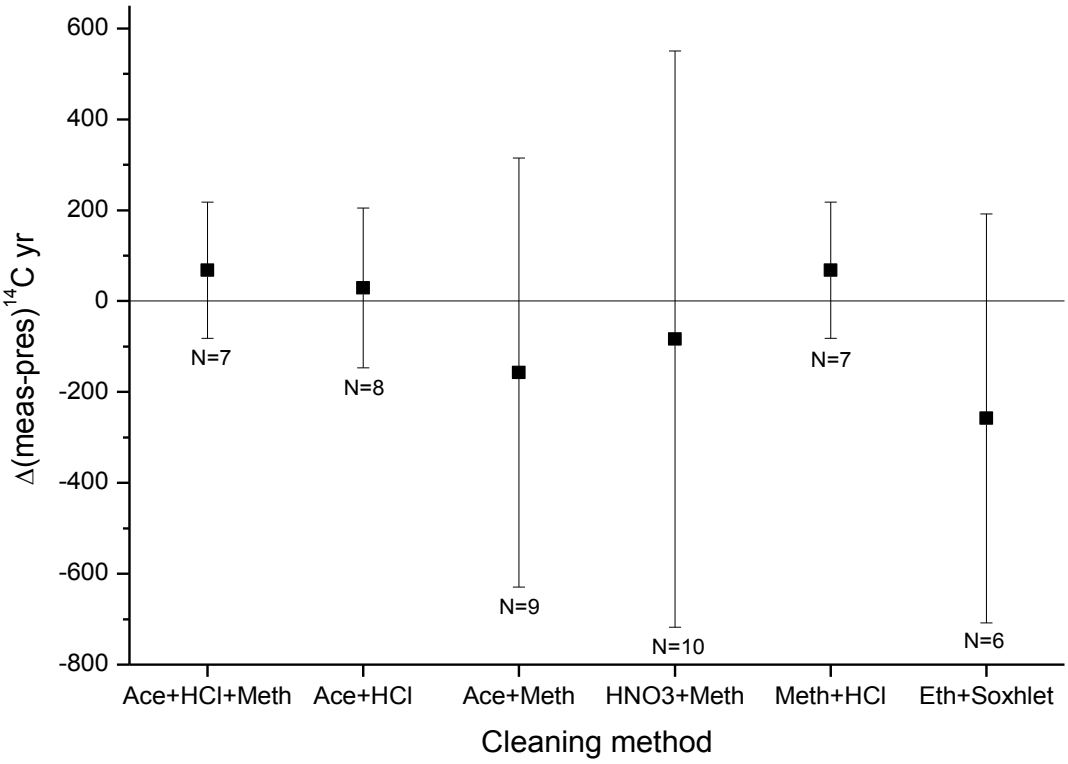


Figure II: Difference between measured and presumed ages for different sample cleaning methods. Mechanical cleaning was not counted as a variable because it was used in most cases. N = number of samples

Based on the earlier dating results, it seems that best pretreatment method for samples is a combination of mechanical cleaning, etching with HNO_3, ultrasonic bath and rinse with de-ionized water and finally ultrasonic bath and rinse with acetone (see Figure II above). Nitric acid is used to remove rust from the sample and acetone for washing the possible remains of cutting oil or other fatty contaminants. Acetone is also used as a final treatment to prevent the re-rust of samples.

5.2 The methods to extract carbon from iron-based materials

There are several different ways to extract carbon out from the iron matrix. Principally there are two main traditions: the dry method and the wet method. Both of these can be divided into several sub-techniques, which are introduced more in detail in the chapters 5.2.1-5.2.4. While laboratories have been developing new methods to date iron-based objects, they have tested their methods with modern, coal-produced iron as reference material. Steel samples are analyzed with elemental analyzer to figure out their elemental composition and carbon contents. These samples have minimum radiocarbon activity (fraction modern = 0,0025 ± 0,0008 or approximately 50 000 BP) and they yield activities which reflect typical laboratory blanks. Reference materials should be used until contamination levels are very low – after that it is safe to start using samples taken from archaeological iron artifacts. (Cook et al. 2001: 222.) If these steel samples contain modern carbon, it is rooted in foundry or it might be adsorbed from the atmosphere (van der merwe 1969: 88).

5.2.1 The dry method

Van der Merwe and Stuiver started an experiment in 1961 to date iron artifacts and iron slag. They developed a method to extract the carbon from iron-based materials and dated the carbon by beta counting. Carbon was extracted from iron with flow-through combustion in oxygen with cryogenic trapping of CO_2. (Cook et al. 2003: 95.)In beta counting the minimum amount of pure carbon needed in the sample was 1 g, which means that with 2 % carbon steel or cast iron sample the whole amount was 50 g. These

amounts were so massive, that artifacts could not be dated without damaging them (Cook et al. 2003b: 16.) The development of accelerator mass spectrometry (AMS) was a great leap for radiocarbon dating. With AMS method the required amount of pure carbon was only 1 mg and sample amounts diminished outstandingly. In 2001 Andrea Cook, John Southon and Jeffrey Wadsworth published a new method to extract carbon from iron. It was based on sealed-tube combustion with CuO in quartz. The method was very simple if compared to its precursors and required materials were available in standard AMS graphite-preparation laboratories, because no gas trapping equipments were required. Needed requisite are quartz tubes, CuO, vacuum lines and an electric furnace capable of reaching 1000 °C. Iron samples were vacuum-sealed in prebaked quartz tubes with CuO and vacuum-sealed again inside larger quartz tubes. The samples were combusted at 1000 °C for 10 hours. The resulting CO_2 was collected by cracking the quartz tube in vacuum and reduced to graphite for AMS measurement. (Cook et al. 2003a: 95-96, 99.)

Mathias Hüls and his research group used Cook´s combustion method in their experiments to date modern iron and steel samples and some iron artifacts with known archaeological ages. In differ to Cook´s method Hüls´s group used CuO together with silver wool for purifying the CO_2. They used the following parameters: (1) *the carbon content of the iron*, (2) *the particle size of the samples*, (3) *the combustion temperature*, (4) *the combustion time* and (5) *the amount of oxygen available via combustion*. Test results showed that only a proper excess of oxygen is needed to yield the best carbon extraction during the combustion – in theory three oxygen atoms are needed to oxidize two iron atoms. (Hüls et al. 2004: 710-711, 714.)

5.2.2 The RF combustion method

Japanese research group started to develop a new carbon extraction system in 1994 at Nagoya University. The carbon was extracted from iron samples by combusting them with a radio-frequency (RF) induction furnace. The samples, a mixture of 1.0 g of pretreated iron sample and 1.0 g of of iron chips were first heated in preheated alumina crucibles at 1000 °C for 10 hours. Then the crucibles and contents were heated at 500°C in an electric oven for 30 minutes in to remove the carbonaceous contaminants from air

dust. After that the samples were taken from the oven and placed into a RF induction furnace, which was connected to a vacuum line system. The vacuum lines were used to purify the resultant CO_2. The samples were heated to melting for 4 minutes in a flow of ultra-high-purity oxygen. The flow rate was 200 mL/min to ensure that all carbon was converted to CO_2. The vacuum system was evacuated in advance for 1 hour and the combustion gas was passed through Pt/CuO at 450 °C to convert any remaining CO to CO_2. Later the CO_2 was condensed with 3 cold traps and cooled by liquid nitrogen and residual gas was pumped out. The remaining CO_2 was separated from water with an ethanol trap at -78 °C, then from any SO_2 that resisted a MnO_2 trap with a pentane trap at -130°C. The amount of CO_2 was measured volumetrically by a manometer. Then the CO_2 was reduced to graphite usable in AMS analysis. (Enami et al. 2004: 222.)

5.2.3 The wet method

There are different ways to extract carbon from iron with chemical pretreatment. The basic idea is to dissolve carbon from iron with acid and $CuCl_2$. The generated precipitate is reduced to a graphite target and dated. Japanese researchers developed a new extraction method in the late 1990´s, which is known as wet or dissolution method. Iron samples were dissolved with HCl and $CuCl_2$ solutions. At first the samples were treated with 4N HCl solution at room temperature for 2 weeks. The carbon residue was collected on quartz wool in a glass funnel. After that the standard iron samples were dissolved in $CuCl_2$ solutions of different concentrations at 60 °C. A mixture of standard iron and $CuCl_2{\cdot}2H_2O$ was added with distilled water to dissolve the iron. The carbon was then precipitated as an aggregated colloid and metallic copper was deposited and dissolved with 4N HCl at 60 °C. The carbon residue was collected on quartz wool by filtration. (Oda et al. 1999: 561-563.) The research group also tested the $CuCl_2$ solution that was filtered through a quartz wool filter before dissolving the standard iron, to eliminate the possible carbon contaminants in the $CuCl_2{\cdot}2H_2O$ solution. (Enami et al. 2004: 224.) Toshio Nakamura and his group also tested another wet method. They used saturated $Ca(OH)_2$ solution and carbon from iron was trapped as $CaCO_3$ and changed to CO_2 by thermal decomposition at 850 °C in a vacuum line. This method was not very effective, only 50-60 % of carbon was collected. (Nakamura et al. 1995: 629-630.)

Myung Ki Cheoun and his Korean research group developed their own version of chemical extraction. The samples were first cleaned with acetone and carbon content was analysed by the element analyser. The samples were dissolved in 0,015M $CuCl_2$ solution at room temperature for an hour. Carbon colloid is known to have a negative charge property, and it can be precipitated with the positive charged Cu^+ ion in $CuCl_2$. The precipitate was dissolved again in 2M HCl for 2 hours to remove Cu from carbon colloid. Process was repeated 6 times until the precipitate begun to turn black. After that the precipitate was washed with distilled water and dried in an oven at 120 °C. Then samples were ready for AMS-analysis. (Cheoun et al. 2001: 218.) Andreas Scarf with his group modified Cheoun´s method and they did not treat samples with $CuCl_2$. Instead, iron pieces were dissolved in 2M HCl at temperature of 85 °C. The precipitate was separated from $FeCl_3$ with a carbon-free glass fiber filter and washed with de-ionized water. After that samples were dried at 100 °C and oxidized in the elemental analyzer and reduced to graphite. This method was very effectual and the efficiency of extracted carbon yield was almost 100 %. (Scharf et al. 2004: 176.)

5.2.4 The direct sputtering

Scharf et al. were the first to test direct sputtering for the radiocarbon dating samples at the Erlangen AMS facility. The method was tested to find alternative carbon extraction technique for samples with low carbon content. If the carbon content is very low, the sample amounts are too large for most combustion systems. Spark erosion technique was used to create an AMS target and replace an ordinary graphite target with it. Ordinary sputter targets consist of a carbon-iron compound, so that direct sputtering of carbonaceous iron is also possible. With direct sputtering targets can be made from unprocessed samples and no combustion or chemical extraction of carbon from the samples is needed. (Scharf et al. 2004: 175-176.) In AMS technique target is bombarded with cesium ion beam and element atoms are sputtered from it. Atoms are ionized by surface ionization, when cesium in its capacity as an alkali presents an electron to sputtered atoms. (Beukens et al. 1999: 297-300.)

Scharf´s group made small pins by spark erosion from the sample material. After cleaning with acetone the pins were directly pressed into a cathode and measured at the AMS facility. The pins had a mass of about 50 mg, which corresponds to 0,5 mg carbon based on a sample containing 1 % C. The technique of direct sputtering is more appropriate for samples with carbon contents of 1 % or above, because the ion current may be too low for samples with very low carbon content. (Scharf et al. 2004: 176, 180.)

5.3 The comparison of the methods

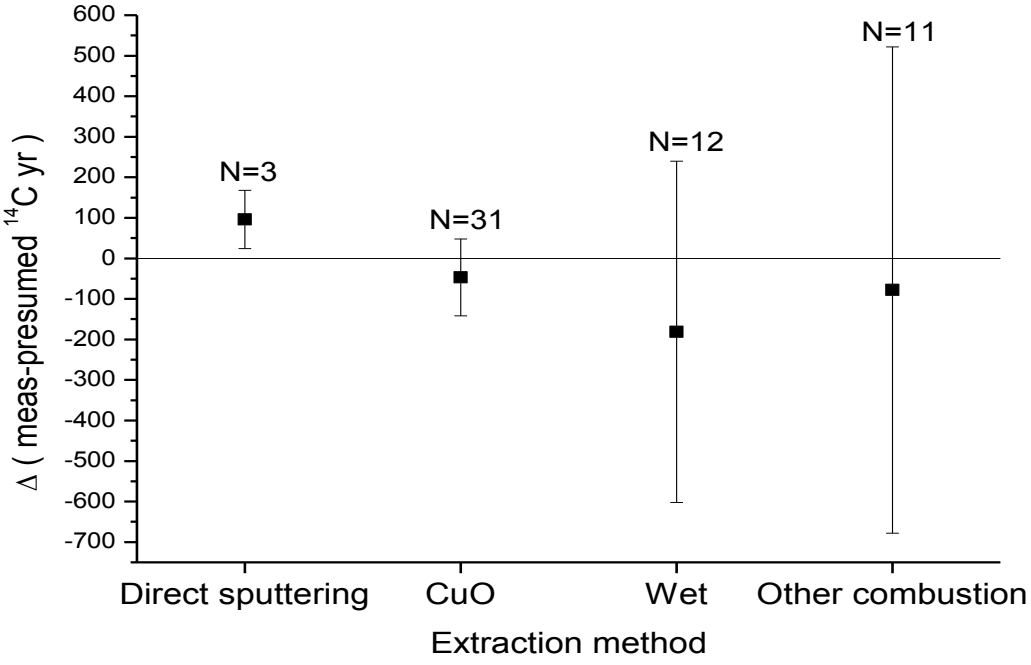


Figure III: Difference between measured and presumed ages for different carbon extraction methods. N = number of samples.

The CuO combustion seems to be the best carbon extraction method – out of the 38 best dates differing less than 100 cal years from the true age, 53 % has been made with the CuO technique (see Appendix: Tables II and III). If comparing all dating results and used carbon extraction methods, the CuO combustion has no equal (see Fig III above and Appendix: Table III). Direct sputtering has also given promising results, but method has not been used very much for this purpose and it needs still more elaboration. From an archaeological perspective the direct sputtering would be a very welcome method, because in theory it enables to analyze the ancient iron artefacts without milling or harming them. This method would also cut down the time that we now spent for the sample pretreatment. At the moment it´s a time-consuming process – the pretreatment of a single iron sample takes now over one week of laboratory work.

6. THE CHARACTERIZATION OF IRON SAMPLES

6.1 The stable isotope measurements

Radiocarbon measurements are always accompanied with a measurement of $^{12}C/^{13}C$-ratio ($\delta^{13}C$) with IRMS -method. These $\delta^{13}C$ aka delta values are used to correct the isotopic fractionation. The $\delta^{13}C$ value is due to material which has ended up into the sample matrix via different processes – these may be natural or caused by human activity. If the iron is smelted with charcoal, it´s delta value should be around -25 ‰. Variations might occur, because high temperatures during the smelting process may impact to delta values. With iron the temperature effect might be significant, because the iron manufacturing process demands temperatures over 1000 °C. The delta values are measured with a mass spectrometer. (Hoefs 2004: 8, 50-53; Taylor 1987: 74.)

6.2 The elemental analyses

Elemental analyses of iron and iron slag are made to measure how iron has been manufactured. In case of radiocarbon dating it is important to measure the carbon content of iron – the required sample amounts vary a lot and they are dependent on the carbon content. The amount of carbon depends on the smelting technique – the maximum is circa 5 %. Wrought-iron contains 0,2 % carbon, cast iron 1,5-5 % and steel 0,1-2 %. (van der Merwe 1969: 5.) If the carbon content is very low, the sample size needed might be too large for some combustion systems (Scharf et al. 2004: 175). Analyses can tell us what sort of ore, fuel and flux type the iron smelters have used during the smelting process. Manganese silicates were often used as the flux and thus Mg indicates the flux material (Craddock 1995: 200.) Slag analyses have revealed that high contents of Ca (>10 %) refer to the use of limestone as a flux. Limestone may dilute the radiocarbon contents of the iron and cause that dating results are older than they really are. (Cresswell 1992: 902.) With a help of elemental analyses we could also inspect the provenance of the iron – such things could reveal is the artifact from The Roman period (The Romans smelted their iron with coal) or is the iron in North America brought there by The Vikings (van der Merwe 1969: 118).

Phosphorus and sulphur usually come from the ore, but also from the fuel (Cresswell 1992: 902). Bark contains even 13 times more phosphorus than heartwood. Phosphorus content is smaller if the trees have been cut down after Midsummer, because the concentration of sap in trees is smaller. In some areas in Estonia ores have really high phosphorus contents – phosphorus debases the quality of iron. (Peets 2003: 35-38). If sulphur contents are between 0,1-0,4 %, coal has probably been used as a fuel. Charcoal contains less than 0.05 % of sulphur, but sometimes it increases iron´s phosphorus content (van der Merwe 1969: 29.). Bog iron and siderite ores may yield sulphur from pyrite (Cresswell 1992: 902). Nickel and copper usually come from the ore, but if iron contains 5-10 % nickel, it is probably meteoric iron (van der Merwe 1969: 14). On the contrary the bloomery iron has a very low Ni content (Chen et al. 2009: 3040). Charcoal usually contains Mg, Ca, K, Sr and Zn, but only zinc may affect to the structure of the metals. Si and Ca rooted from smelting of the metal but Al, Ti and V from the linings of the smelting furnaces. (Craddock 1995:189; Desaulty et al.2008: 1253-1262).

Typical methods for elemental analyses of iron samples are electron microscopy, Particle-induced X-ray emission (PIXE) (see Rueter et al 1975) and X-ray fluorescence (XRF) (see Beckhoff et al 2006). In Aikarauta project we measured our samples with XRF, ICP-OES and ICP-MS techniques. These methods will be discussed more in detail in chapter 7.6.

7. THE AIKARAUTA-PROJECT

In this chapter I will describe the Aikarauta-project´s laboratory work in detail. All together, we investigated 20 different iron samples. Two of these were reference steels from Rautaruukki, four were modern iron cakes which were smelted with the ancient technique. The rest 14 samples came from different archaeological contexts. Samples with Hela-code were dated in Tandemlaboratory (University of Uppsala, Sweden) and HelaH-samples in Accelerator Laboratory (Department of Physics, University of Helsinki). The samples were prepared in Dating Laboratory (Finnish Museum of Natural History, University of Helsinki) by senior laboratory technician Anne-Maija Forss, preparator Heidi Nordqvist and postgraduate Antti Kaskela. The delta values were measured by laboratory engineer Igor Shevchuk.

7.1 The reference samples:

7.1.1. The industrial samples

Harri Leppänen from Rautaruukki Oyj supplied us modern steel samples as reference material. Steel is produced with fossil fuel and its carbon amount is known. These steel samples were used as “the zero samples” and we used them to test our background and the possible traces of contamination coming from our pretreatment process. Because these samples contain no radiocarbon, possible amounts of it would come from laboratory treatment or from the milling of the iron. The carbon content of the reference samples varied from 0.13 to 4.7%. (Oinonen at al. 2009 s. 875-876.)

RR 1 (Hela 1646):
A reference sample from Rautaruukki Oyj. Iron is produced with coal and has a minimum amount of radiocarbon. These samples were used to test the accuracy and contamination risks in sample milling – if there is any evident of radiocarbon in the dating results, it´s a cue of contamination

.

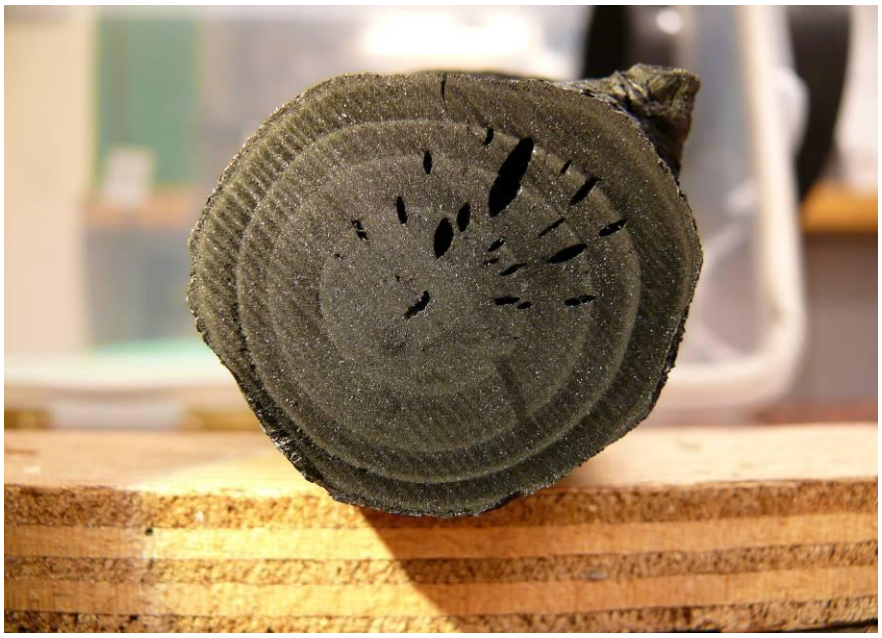
RR 6 (HelaH 26, HelaH 27, HelaH 28, HelaH 29):
Carbon steel from Rautaruukki Oyj, used as a reference sample. Iron is produced with coal and it has a minimum amount of radiocarbon. This sample was used to test can we loosen the carbon from iron and test the contamination risks. Sample contained 4 % of carbon. We milled 50 mg iron for a sample, which generated as a result a 1.5 mg carbon target. Sample´s ^{14}C-concentration was very close to the typical radiocarbon background, as presumed.

7.1.2. The homemade iron

Aikarauta project also produced four different iron cakes: the iron smelting experience in Hamina was supervised by blacksmith and an amateur archaeologist Seppo Kallio. Iron was smelted by following the over 200 year old recipe of Carl Rinman (Rinman 1794), a quote from his guidebook for rustic iron manufacturing process. Smelting furnace was built of light gravel blocks and lined with clay. Furnace was filled from above with carbon, roasted iron ore and pulverized flux. Air was blown inside the furnace with a pipe underarm, with a help of an engine-generator. Slag was trickled out from the furnace via a small hole. Furnace was pulled down after the smelting and iron cakes were split in half with an angle grinder. All materials were dated with AMS method: charcoal, iron ore, limestone flux and four iron cakes.

KK 1 (HelaH 22):
This sample was limestone ($CaCO_3$), ground up by mortar and pestle and used as a flux in the smelting process of OMA 1 iron. Limestone is composed of fossil carbonate and it contains no radiocarbon. When limestone is mixed with charcoal and iron ore, it brings stable carbon $^{12,13}C$ into iron and dilutes sample´s original radiocarbon content. Stable carbon adds years to radiocarbon dating results, and we tried to measure this effect by adding a certain amount of $CaCO_3$ into smelting furnace.

MA 1 (HelaH 24):
Iron ore for smelting process of OMA irons. This contained also pieces of charcoal from roasting process.



Picture 6: Charcoal (HelaH 25) sample.

PH 1 (HelaH 25):
Charcoal, made of young wood with known age (max. 10 years). Used for smelting of the OMA irons.

OMA 1 (Hela 1659):
Iron cake, smelted for Aikarauta project. Iron is made with 5.7 kg of charcoal, 6.3 kg of iron ore and 0.44 kg of pulverized limestone as a flux. Constituents were added into furnace at 10-minute intervals. The smelting process took in its entirety 1.5 hours and resulted 0.8 kg of iron and approximately 5.5 kg of slag (KU 3). This sample is used for testing how limestone effects to dating results.

OMA 2 (HelaH 54):
Iron cake, smelted for Aikarauta project. This iron was made with 4067 g of iron ore and 4164 g of charcoal, no flux was added. Smelting produced an iron cake of 2500 g in weight. Because no flux was added, no slag was formed during the smelting process.

OMA 3 (Hela 2000):
Iron cake, smelted for Aikarauta project. This iron was made with 3390 g of iron ore and 3956 g of charcoal. It contains 181 g of quartz sand as a flux. Smelting process resulted 718 g of iron.

Picture 7: OMA 3 iron cake, cut in two pieces.

OMA 4 (HelaH 73):

Iron cake, smelted for Aikarauta project. Quartz sand flux.

KU 3 (HelaH 33):

Slag from smelting process of OMA 1 iron. Slag was crushed with vice, mortar and pestle. We tried to date crushed slag, which proved to be a very challenging project. The slag contained so much impurities and silica that the quartz ampoules were corroded by slag. Sample could not be analyzed for ^{14}C.

7.2 The archaeological samples:

We managed to receive plenty of sample material from our partners in cooperation, who were archaeologists Georg Haggrén, Risto Karasmaa, Andreas Koivisto, Henrik Jansson, Mika Lavento and Jüri Peets. The samples were mostly iron nails, but we also tested pieces of other artifacts and iron slag. The slag was very problematic material, because it contained so much silica, that it reacted with quartz tubes – the quartz glass actually turned into slag because the sample contained so many impurities.

JP 1 (HelaH 36):
Iron sample from Tuiu, Estonia. Age estimation was 1200-1400 A.D. Pre-industrial Estonian iron may contain fossil carbon, because local soil is very calciferous.

JP 3 (HelaH 37):
Iron sample from Raatvere, Estonia. Age estimation was 1200-1400 A.D.

JP 4 (HelaH 38):
Iron sample from Tuiu, Estonia. Age estimation was 1200-1400 A.D.

KU 1 (HelaH 23, HelaH 31, HelaH 32, Hela 1322, Hela 1640, Hela 1655, Hela 1656):
Iron slag from Paaskoski, Ruotsinpyhtää. Slag was crushed with vice, mortar and pestle. We tried to date charcoal found inside the slag and crushed slag.

Gubbacka 1 (HelaH 40):
Iron nail from Gubbacka´s medieval village site. This site was really interesting, because there are small lime workings in the surrounding neighbourhood.

Gubbacka 31 (Hela 1993):
Iron nail from Gubbacka´s medieval village site. This sample had an oat grain (Hela 1994) as a reference sample.

Gubbacka 45 (Hela 1995):
Iron nail from Gubbacka´s medieval village site. This sample had a rye grain (Hela 1996) as a refence sample.

China 1 (Hela 1997):
Chinese iron coin with known period of manufacture, made of cast iron. The coin goes back to AD 1086-1100, the reign of Northern Song dynasty.

China 2 (Hela 1998):
Chinese iron coin with known period of manufacture, made of cast iron. The coin goes back to AD 1086-1093, the reign of Northern Song dynasty.

Salme 5 (Hela 2149):
Iron nail from a ship burial from Saaremaa, Estonia. Age estimation is Pre-Viking Age.

Salme 27 (Hela 2150):
Iron nail from a ship burial from Saaremaa, Estonia. Age estimation is Pre-Viking Age.

Salme 14 (Hela 2520):
Iron nail from a ship burial from Saaremaa, Estonia. Age estimation is Pre-Viking Age.

SM 10601:78 (Hela 2521):
Iron sample from Estonia.

KM 2007056:345 (Hela 2530):
Iron nail from Gammelby dwelling site from Inkoo. Age estimation is medieval.

KM 2008088:288 (Hela 2531):
Iron nail from Gammelby dwelling site from Inkoo. Age estimation is medieval.

7.3 The sample pretreatment protocol

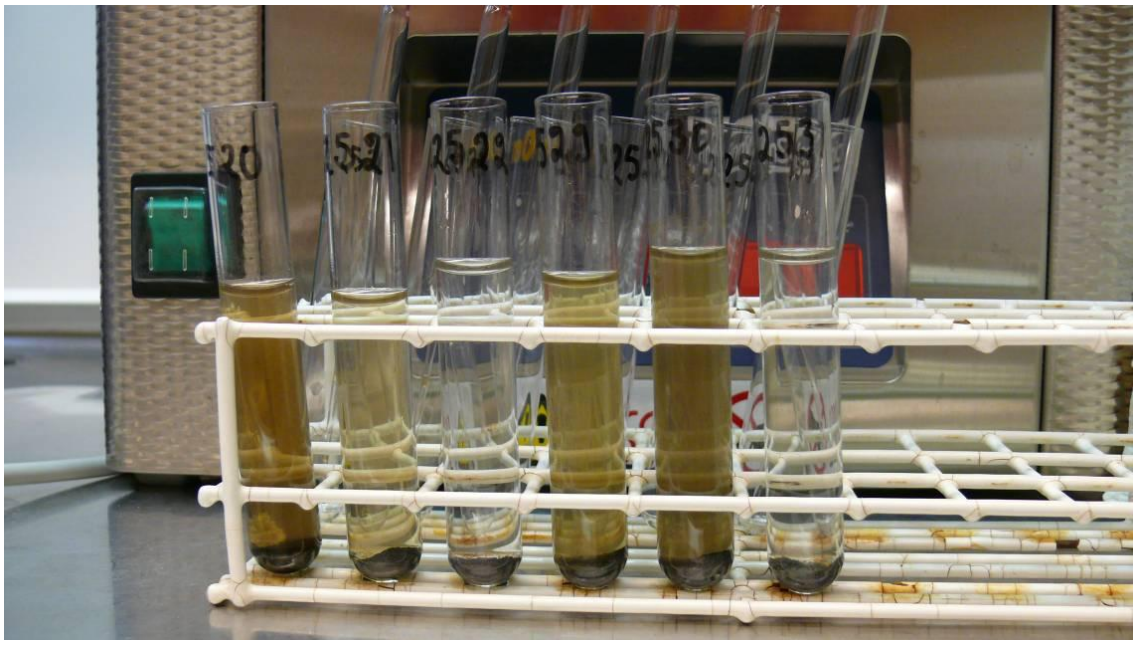
The sample pretreatment protocol that we are using for iron is based on the copper oxide combustion method developed by Cook (Cook et al. 2001:221) and Hüls (Hüls et al. 2004:710).

Step	Treatment A-1	Treatment A-2	Treatment B	Treatment C
Mechanical			Polishing by Al2O3	Polishing by Al2O3
cleaning			wheel	wheel
Sampling	Milling machine + oil	Milling machine + oil	Grinding by Al2O3	Grinding by Al2O3
	(chips)	(chips)	wheel (grains)	wheel (grains)
Cleaning_1	Toluene 12 h	Toluene 12 h	H2O × 2	H2O × 2
Cleaning_2	Toluene + US 15 min	Toluene + US 15 min	H2O + US 15 min	H2O + US 15 min
Cleaning_3	(Acetone + US 15 min) x 2	(Acetone + US 15 min) x 2	H2O × 2	H2O × 2
Cleaning_4	Acetone rinse × 2	Acetone rinse × 2		Acetone rinse
Cleaning_5		10% HNO3 etching		Acetone + US 15 min
Cleaning_6		H2O rinse until neutral		Acetone rinse
Cleaning_7		EtOH		
Drying	@ 90 °C	@ 90 °C	@ 90 °C in vacuum	@ 90 °C in vacuum

Table 1: Sample pretreatment variations for RR-iron samples. Treatment C is used for all archaeological sample material. US = ultrasonic bath. (Oinonen et al.2009: 876) The pretreatment protocol has been developed since publication of the paper as described below.

To minimize the risk of contamination, all working tools and surfaces are cleaned with acetone before sample pretreatment. Abrasive discs and the attaching screws are washed in ultrasonic bath with acetone to remove all possible remains of grease. The samples from archaeological contexts (iron nails) are usually badly corroded and covered by thick corrosion layer, mixed with sand and clay. This layer can be removed carefully with a curet and aluminium oxide (Al_2O_3) abrasive disc. The rust is recovered in case of possible subsequent tests and dating experimentation with rust, if we´d like to test how results differ cleaned and rusty samples.

After cleanse the sample is milled with Dremel multitool and an abrasive disc. The abrasive disc is exchanged for a new one after use to avoid possible contamination with rust. Some samples had very high carbon content, which caused serious problems with Dremel multitool. Dremel´s revolution speed was too high and it induced sparks when abrasive disc hit the sample´s surface - a spark can ignite the iron powder inconveniently in fire. For this reason we purchased another multitool (Proxxon) with lower revolution speed. However, sparks also have its uses and a spark test is very useful when iron´s carbon content is estimated without elemental analyses. Those samples, which carbon contents were very high, were milled with Bosch drilling machine, because it´s revolution can be adjusted manually to a lower level. Because of the risk of spark, milling of 2 grams of iron powder took hours. Milled iron powder is collected by means of a strong magnet and weighing paper. At this point the possible remains of Al_2O_3 powder which came off from the abrasive discs are separated from iron powder with a magnet.



Picture 8: Iron samples in acetone wash.

In the next phase samples are weighed and put into test tubes, which are numbered with our laboratory´s Hela-code. Samples are rinsed with distilled water and washed for 15 minutes in ultrasonic bath to remove the possible impurities. After this water is pipetted off and the samples are rinsed with acetone and washed for 15 minutes in ultrasonic

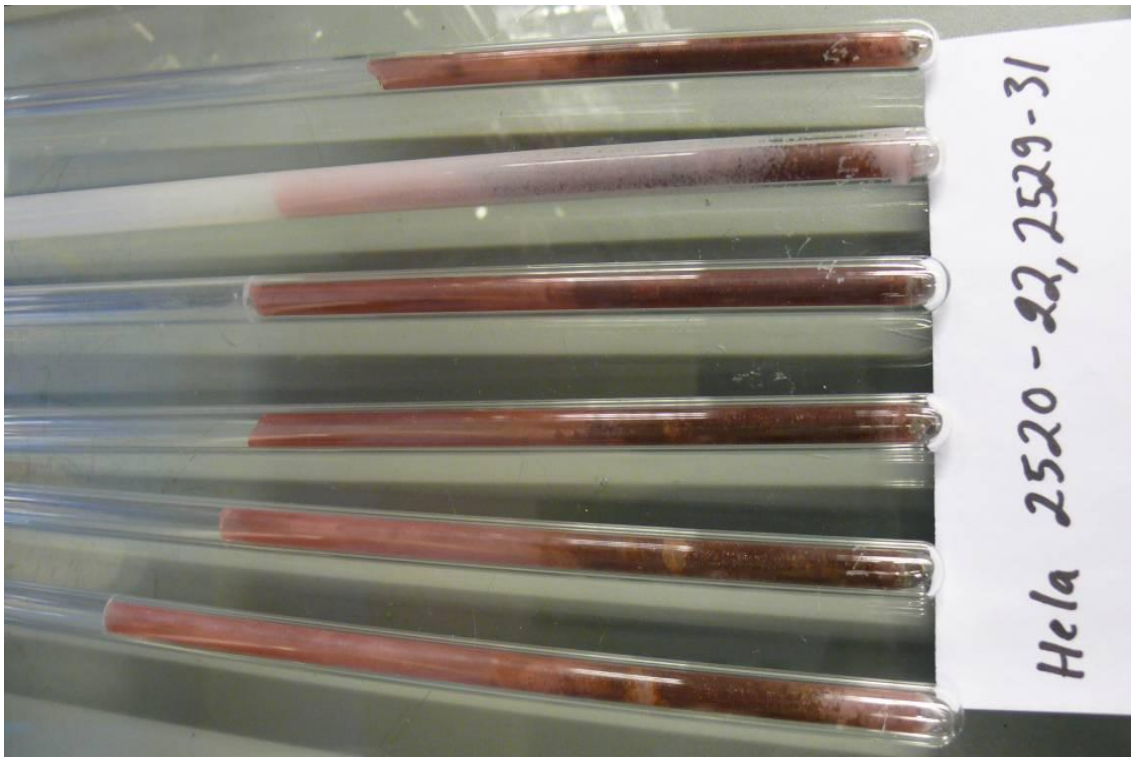
acetone bath. Samples are rinsed with acetone until the liquid is bright and then acetone is pipetted off. Acetone protocol is followed to prevent the samples growing rust. Samples are dried in +90 ºC over night in a vacuum oven. After drying the samples are weighed and packed into Hela-numbered eppendorf-tubes to wait for handling to continue. Prepared samples are kept in the desiccator closet.

7.4 The carbon extraction protocol

Preparation of iron samples differs a little from the typical radiocarbon sample pretreatment protocol. Samples are packed into quartz ampoules – the ampoules are roasted before use in 1000 ºC for one hour. Copper oxide must be also roasted (860 ºC for one hour) every time before use to remove crystal water. If sample´s carbon content is unknown, we weigh 250 mg CuO per 1 mg of sample. Hüls (Hüls et al. 2004:709) used Cu_xO/Fe ratio >5 (by weight). It is even better to have surplus of copper oxide. Samples and CuO are mixed with spatula and packed into quartz ampoules. Iron powder and quartz glass may together set up static electricity, which can be reduced with an ionizer. If the iron powder does not mix with CuO, mixing can be eased with a magnet. It´s really important to make sure that iron powder is mixed properly, otherwise the combustion will be incomplete. If it is known that iron may contain sulphur, it is good to add some silver wool into the quarts ampoules (A-M Fors 2011, personal communication.) After this ampoules are pumped into vacuum in the vacuum line and sealed by welding. Ampoules are roasted for 10 hours (usually overnight with a timer) in an oven in temperature of 1000 °C. The sample contains carbon, which reacts with CuO: the copper oxide reduces and cedes an oxygen atom, while carbon becomes oxidized. This is known as combustion reaction, which constitutes carbon dioxide (CO_2).

Next morning, after cooling off, the ampoule is connected to vacuum line and the possible impurities (like water) are separated from the carbon dioxide with liquid nitrogen and ethanol baths. The method is based on the temperature differences: at first the carbon dioxide is transformed into dry ice by force of liquid nitrogen (-196 °C). Temperature of the ethanol bath is “only” – 85 °C, which is enough to liberate the CO_2 but the impurities still remain bounded in the ice. If the colour of a quartz tube is a bit

yellowish, the sample may have higher sulphur content. In such cases it is important to purify the gas twice or three times. Too much sulphur impacts to graphitization process and CO_2 fails to reduce properly. After CO_2 is purified, it is transferred into an ampoule and it´s $\delta^{13}C$ value will be measured with a mass spectrometer. Finally the carbon dioxide is reduced back to carbon with zinc and iron powder: in the reduction reaction the zink powder receives oxygen from CO_2. Iron powder is used as a catalyst and carbon reduces on the powder´s surface. The samples are graphitized in special graphitization ovens. After this process the carbon-iron samples are weighed, compressed into carbon targets and ready for AMS-measurements.



Picture 9: Iron samples in quartz tubes after combustion in 1000°C. The second tube from the top is almost white, which means that quartz glass has reacted with the impurities of the sample and the tube is so corroded that it´s nearly broken.

7.5 The AMS measurements

The Aikarauta samples were analyzed with two different accelerators. The samples with HelaH-code were dated in Accelerator Laboratory in Helsinki and Hela coded materials in Tandemlaboratory in Uppsala. At the beginning we had an idea to date all sample materials in Helsinki, but Tandemlaboratory had a better accuracy for younger samples at that time. During the HelaH 36-HelaH 40 sample measurements there was also some drifting in the accelerator, so it was necessary to test all of the possibilities. The Helsinki accelerator has a background which is actually more suitable for older samples, like geological sediment materials. The Helsinki Accelerator has also been out of use because of the renovation, which is another reason why we had to send our samples to Tandemlaboratory. The radiocarbon results are given in units of BP (before present) and absolute percent modern carbon (abs pMC) as defined in (Stuiver and Polach 1977).The unit abs pMC shows essentially the amount of radiocarbon relative to the year 1950 level. Typically, the raw radiocarbon ages provided by the AMS facility has been corrected for radiocarbon background of 38000 ± 2000 BP and for isotopic fractionation unless otherwise mentioned.

7.6 The elemental analyses of The Aikarauta samples

One of my main aims with this research was to chase up is it possible to trace via elemental analysis how the iron is manufactured. We wanted to test this hypothesis by comparing the contents of Ca, S, Mg, C, Ni and P. At first we sent our RR-reference samples to University of Jyväskylä (Ambiotica by Allan Witick), where the materials were analyzed with ICP-OES-technique. The following elements were analyzed: Ca, Cr, Co, P, Mn, Ni, Si, Ti and V. The Rautaruukki Company analyzed the RR-6 samples elements with X-ray fluorescence -method (XRF). Most of the archaeological material, altogether 14 samples were analyzed in Helsinki with ICP-MS-technique, where the following elements were analyzed: Mg, Si, P, Mn, Fe, Co, Ni, Cu, Zn, As, Sn, Sb, Pb.

With the ICP-OES-technique samples were pretreated by soaking the iron powder in HNO_3/H_2O_2-solution. The ICP-MS-pretreatment was produced by microwave digestion, which is an excellent method for soil samples, but the metallic samples caused a lot of

extra work for laboratory personnel. The Aikarauta-samples contained too much silica: the silica blocked the ICP-MS-instruments cone so many times that the laboratorians were forced to dilute the samples and Ca was also precipitated off. The results of the elemental analyzes were run with the R-programming language to see if the samples would form any clusters, which would show their different origins.

8. THE RESULTS AND DISCUSSION

8.1. The reference samples

The radiocarbon ages of the reference samples are not converted into calendar years, because these samples contain fossil ingredients or they gave a modern dating result. The method to date iron-based materials is still under development in our laboratory and therefore we hesitate to give calibrated for these samples.

Lab.No	Sample	$\delta^{13}C$(‰)	Radiocarbon age (BP)*	abs pMC *	Notes
Hela-1641	RR-6	-24,9	34240 ± 150	1,4 ± 0,1	in Upps
same	RR-6		32380 ± 480	1,8 ± 0,2	in Hels
Hela-1646	RR-1	-23,9	23560 ± 80	5,2 ± 0,1	in Upps
same	RR-1		22480 ± 310	6,0 ± 0,3	in Hels
HelaH-28	RR-6	-25,0	30950 ± 300	2,1 ± 0,1	
HelaH-29	RR-6	-24,9	33850 ± 310	1,5 ± 0,1	

Table 2: The results of the RR-reference iron samples.

As we expected, the reference steel samples gave the results that are very close to the adopted background level (38000 BP). These samples are manufactured with coal, so they should contain no radiocarbon. However, it is possible that small amount of radiocarbon observed (1-2 % from the year 1950 level) is due to steel manufacturing process and resulting from the ambient CO_2 in the air used in the smelting process. The dating result for Hela-1646 is much younger than Hela-1641, but this may derive from different pretreatment method or the very small carbon contents of the RR-1 sample.

Lab.No	Sample	$\delta^{13}C$(‰)	Radiocarbon age (BP)	abs pMC
Hela 1659/1	OMA-1 iron	–26,2	2330 ± 120	77,3 ± 1,1
Hela 1659/2	OMA-1 iron	–25,1	2060 ± 110	74,8 ± 1,1
HelaH 54	OMA-2 iron	–17,2	>MODERN (-652 ± 66)	108,5 ± 0,9
Hela 2000	OMA-3 iron	–25,9	>MODERN (-655 ± 35)	107,7 ± 0,5
HelaH 73	OMA-4 iron	–26,9	>MODERN (-617 ± 47)	108,0 ± 0,6

Table 3: The results of the OMA reference iron samples.

OMA iron cakes were smelted with the ancient manufacturing technique by using <10 year old charcoal (wood). Therefore, their radiocarbon content should reflect the modern atmospheric content of around 105 pMC units. OMA-1 iron showed very small radiocarbon content which indicates that it results of a mixture of charcoal and carbon source having less radiocarbon. One possibility is the limestone flux, which dilutes the radiocarbon content. OMA-2 iron´s delta value is really strange, but this iron was smelted without any flux and this may have effect to the temperature of the furnace and the iron´s smelting point, as well. OMA-3 and OMA-4 iron cakes were smelted by using quartz sand as a flux. Overall, the result look reasonably good: they show that modern radiocarbon contents will be observed for iron smelted with modern charcoal. In addition, there is a sign for incorporation of older carbon in case of limestone flux.

8.2. The archaeological samples

8.2.1. The Gubbacka iron

Lab. No	Sample	$\delta^{13}C$(‰)	^{14}C age (BP)	Calendar age 1σ (AD)	Ref.age (AD)
Hela-1993	Gubbacka, iron nail 31	-22,9	1085 ± 35	895-925	1100-1500
Hela-1994	Gubbacka, soil sample 6 (carbonized oat grain)	-25,0	480 ± 35	1415-1445	1100-1500
Hela-1995	Gubbacka, iron nail 45	-21,4	800 ± 35	1215-1265	1100-1500
Hela-1996	Gubbacka, soil sample 11 (carbonized rye grain)	-25,9	1515 ± 40	440-490	1100-1500
HelaH 40_1	Gubbacka, iron nail	-21.9	940 ± 105	1010-1210	1100-1500
HelaH 40_2	Gubbacka, iron nail	-22,3	890 ± 100	1030-1220	1100-1500
HelaH 40_3	Gubbacka, iron nail		914 ± 72	1030-1180	1100-1500

Table 4: The results of the Gubbacka iron samples and the reference samples.

Iron samples from the medieval Gubbacka dwelling site were quite challenging material. Gubbacka was habited in the period of 1100-1500 AD. We were prepared to get much older dating results, because nearby the site there are many old limestone

workings. If the soil is very calciferous, the iron may contain fossil carbon. If the iron is produced locally, the fossil contamination may origin from the ore or even from the local wood which is used as charcoal during the smelting process. Limestone can also be used as a smelting agent. Surprisingly, only one sample, Hela-1993 gave remarkably older result (895-925 AD). All of the Gubbacka iron samples were iron nails and my humble opinion is that nails are not a suitable material for radiocarbon dating of iron. Nails are probably re-forged and recycled – when a house is pulled down, nails are collected and re-used. If they are bent, the blacksmith may have re-forged or straighten them in the smithy, where the main fuel has usually been coke.

We dated two carbonized grains as the reference samples for the iron samples. These oat and rye grains came from the same context as the iron nails, so they should give quite similar dating results. Unfortunately the samples did not matched – as the iron sample Hela-1995 result was AD 1215-1265, the reference rye grain Hela-1996 dated back to The Migration Period (AD 440-490). In proportion the iron nail Hela-1993 dated back to The Viking Age (AD 895-925), but the reference oat grain Hela-1994 was from The Late Middle Ages (AD 1415-1445). It is hard to say why these results crossed – many evidences show that the Gubbacka dwelling site had habitants already in the Iron Age. Cultivation of soil also mixes the soil layers and even moles may deliver archaeological items from place to place in their tunnels.

8.2.2. The Gammelby iron

Lab.No	Sample	$\delta^{13}C$(‰)	Radiocarbon age (BP)	Calendar age (AD)
Hela-2530	KM 2007056:345	-25,8	1080 ± 32	895-1015
Hela-2531	KM 2008088:288	-23,3	1189 ± 32	780-885

Table 7: The results of the Gammelby iron samples.

The samples from the Gammelby dwelling site in Inkoo were two iron nails. The first signs of settlement are based on pollen analyses and date back to AD 400-500 , but most of the find materials are dated to be medieval. The samples gave a few hundred years older ages than we expected and the reason is probably same as it was with the Gubbacka´s materials. Nails are often re-used, re-forged and recycled – even if the

blacksmith would have used only charcoal-based fuels in the smithy, the own age of iron may be around 200 years. These samples were also very rusty, which may also have taken effect to the dating results. The quartz tube for the sample Hela-2530 was almost white after combustion, which is a sign of impurities. It may be silica, which has reacted with quartz glass – the iron is possible smelted by using quartz sand as a flux.

8.2.3. The Estonian iron

Lab.No	Sample (ref)	$\delta^{13}C$(‰)	^{14}C age (BP)	Cal. age (AD), 1σ	Ref age (AD)
HelaH-36	Tuiu-A1 (Tln-1225)	-30,7	1130 ± 100	770-1020	1260-1390
HelaH-37	Raatvere (Tln-633)	-28,9	1390 ± 105	550-770	890-1020
HelaH-38	Tuiu-A1 (Tln-1225)	-28,3	720 ± 105	1210-1330	1260-1390
Hela-2149	Salme nail 5	-24,5	5813 ± 40	abs pMC ~ 48	700-900
Hela-2150	Salme nail 27	-22,1	2705 ± 31	abs pMC ~ 71	700-900
Hela-2520	Salme nail 14	-23,0	2485 ± 31	abs pMC ~ 73	700-900
Hela-2521	SM 10601:78	-22,8	3797 ± 33	abs pMC ~ 62	

Table 6: The results of the Estonian iron samples.

The age estimations for Tuiu samples were 1260-1390 AD and of Raatvere sample 890-1020 AD based on existing radiocarbon measurements from the sites (Peets, private communication). All the results except HelaH-38 (Tuiu) were older than we had expected and refers that the iron might be re-forged and the blacksmiths may have used coke as a fuel. The Raatvere sample (HelaH-37) was seriously rusty and since we have not been treating rusty samples before, we can´t rule out the effect of it on the result.

We had quite high hopes for the samples Hela-2149, Hela-2150 and Hela-2520: these came from a ship burial from Salme, Estonia (see Konsa et al. 2009: 213-222). The preliminary age estimation for the ship is around AD 700-900, the Pre-Viking Age. This material was extremely fascinating, because we also received bone and antler gaming pieces from the same context. The results were very surprising as they all showed significantly older ages than expected. This is even more significant due to the fact that analyses were performed in two batches: both gave too old results. The radiocarbon

amounts and ages indicate a source of old carbon to play a role. Possible sources might be coal/coke and peat as a fuel and/or limestone as a flux. Since the ages are thousands of years, we exclude purely fossil source of fuel. An intriguing possibility of peat may even allow studies of origin of the boat, since peat was not used commonly for iron smelting – or then the blacksmith has forged the nails by using coke as a fuel.The results of the samples Hela-2149, Hela-2150, Hela-2520 and Hela-2521 are not converted into calendar years, because these samples are clearly not realistic.

8.2.4. The Chinese iron coins

Lab.No	Sample	$\delta^{13}C$(‰)	^{14}C age (BP)	Cal. age (AD), 1σ	Ref age (AD)
Hela-1997	China iron coin	–21,7	29485 ± 685		1086-1100
Hela-1998	China iron coin	–26,2	1120 ± 40	885-980	1086-1093

Table 7: The results of the Chinese iron coin samples.

Chinese iron material gave us a big surprise: we expected, that iron would have been smelted with coal, but only one of the two samples actually was. These samples were really special, because we knew the actual date of manufacture. Hela-1997 was sminted in AD 1086-1100, but the use of fossil coal gave us very different dating result. Hela-1998 was minted in AD 1086-1093, so its dating result had an error of 150 years compared to the manufacturing date. This is a very encouraging result and shows that cast iron artefacts might be useful material for radiocarbon dating, because this material was not re-smelted or re-forged.

8.3. The characterization of the samples: the elemental analyzes

The Aikarauta project was started by having the elemental analyzes done with the ICP-OES-technique. We wanted to test what sort of elements our reference steels and OMA-1 iron and its components would contain. At the beginning the project was tracking how much the use of limestone as a flux would effect on the radiocarbon dating results. In table 8 we can see that OMA-1 iron has very high calcium content (6300 mg/kg). Particularly, the high Ca content was found from the limestone-driven slag (Oinonen et

al.2009). As the research went forward, the interest was attracted by other challenges as the limestone was not considered the main problem in the early iron smelting in Finland (internationally the situation might be different).

Hüls et al. (Hüls et al 2011: 151-160) brings in that the error of a few hundred years in the dating results would come from contamination, caused by the modern steel tools that are used in the laboratories during the pretreatment process of the iron samples. This is possible, but more likely we are on the right track if we try to trace how much the early blacksmiths used of coke in their forges. In Korea the metallurgist and archaeologist (see Park et al. 2008: 2465-2470) have traced very high sulphur contents from Mongolian iron and they suggest that it is an indication of the transition from charcoal to coal. I contacted Jang-Sik Park, the professor of metallurgy in Hongik University and we discussed is it possible to trace any signs of the use of coke via elemental analyses. Sulphur was the key element (expect the Chinese samples, because Chinese mineral coal contains only a bit sulphur!). As mention earlier, we wanted to test is it possible to get any information of the manufacture process of iron with a help of the elemental analyses, so we wanted to compare the contents of Ca, S, Mg, C, Ni and P.

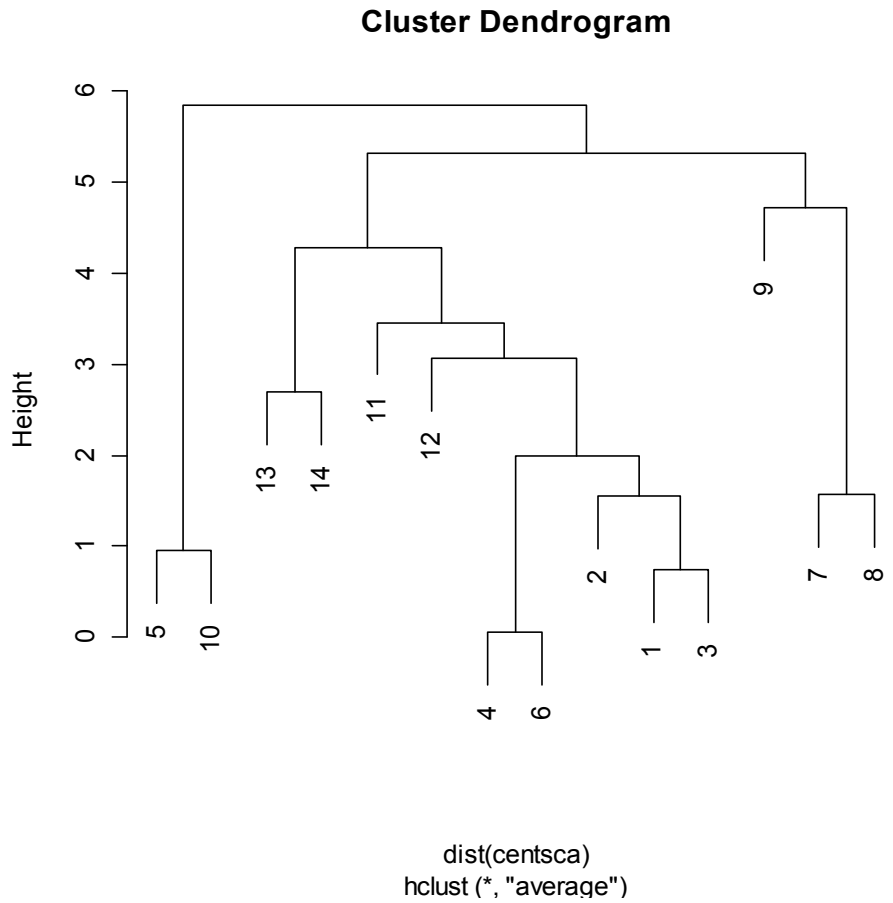
Lab. No	Sample	Mg	Si	P	Mn	Fe	Co	Ni	Cu	Zn	As	Sn	Sb	Pb
HelaH 36	1	NA	1693	NA	656	913	29	61	NA	NA	719	NA	1	NA
HelaH 37	2	NA	1093	3166	492	927	54	40	NA	7	315	NA	NA	NA
HelaH 38	3	21	NA	NA	79	918	37	24	NA	NA	853	NA	NA	NA
HelaH 40	4	80	NA	152	267	939	50	14	NA	NA	21	NA	NA	NA
Hela 1993	8	NA	NA	NA	NA	808	NA	12	NA	NA	NA	17	63	NA
Hela 1995	9	NA	NA	NA	NA	NA	NA	16	NA	NA	NA	15	67	NA
Hela 1997	10	78	3172	1138	6656	884	35	198	0	6	1145	NA	976	NA
Hela 1998	11	26	1858	1205	6919	912	36	216	0	NA	1199	3	1009	6
Hela 1659	12	111	4121	348	166	879	41	469	1	11	1119	4	NA	12
HelaH 54	13	217	7321	349	79	818	12	50	NA	9	628	NA	NA	NA
Hela 2000	14	85	4727	462	547	927	29	53	NA	5	1608	NA	NA	108
HelaH 73	15	101	3811	320	90	893	21	49	0	9	656	3	NA	5
Hela 2149	16	147	4230	1297	303	911	330	174	0	NA	151	NA	NA	NA
Hela 2150	17	82	2032	1316	170	932	219	82	0	8	45	NA	NA	NA

Table 9: The results of ICP-MS elemental analysis. NA = not available.

HNO3 + H2O2 soaking & ICP-OES				
	Concentration (mg/kg)			
Sample	**Ca**	**Cr all**	**Cu**	**Pb**
MA-1	4100	21	2	15
KK-1	360000	<1	<1	<3
KU-3	26000	15	40	11
RR-6	<30	240	34	27
OMA-1	6300	9	25	440
Rautaruukki measurements		**XRF**		
	Concentration (%)			
Sample	**Ca**	**Cr all**	**Cu**	**Pb**
RR-6		0,031	0,01	
	Concentration(ppm)			
RR-6	0	310	100	0

Table 8: The results of the elemental analysis of the reference materials. Measurements were followed through by ICP-OES and XRF techniques. OMA-1 iron was smelted with limestone flux, which explains the irons high calcium content.

An attempt to measure elemental contents of archaeological samples was performed with the ICP-MS technique. Unfortunately, it was noticed that the ICP-MS-technique is not very suitable for metallic samples. Iron contained so much silica that it caused technical problems, eventually it was needed to dilute the samples so much that most of the elements could no longer be defined. Particularly, Ca was completely precipitated off from the samples. In addition, the contents of C and S cannot be measured by ICP-MS-technique. These elements should be measured separately with a carbon-nitrogen-sulphur analyzer. Therefore the outcome of the elemental analyses was reduced to a survey on whether the data could be used to obtain information on the origin of the iron samples.



R-run number	Lab. No	Site	Flux
1	HelaH36	Tuiu	
2	HelaH37	Raatvere	
3	HelaH38	Tuiu	
4	HelaH40	Gubbacka	
5	Hela-1993	Gubbacka	
6	Hela-1995	Gubbacka	
7	Hela-1997	China	
8	Hela-1998	China	
9	Hela-1659	OMA-1	lime
10	HelaH 54	OMA-2	no flux
11	Hela-2000	OMA-3	quartz sand
12	HelaH 73	OMA-4	quartz sand
13	Hela-2149	Salme	
14	Hela-2150	Salme	

Table 10: A cluster analysis of the iron samples, based on the ICP-MS elemental analysis results. Cluster analysis by Markku Oinonen 2010.

We run the ICP-MS-data with R to see is it possible to form different clusters – this worked out reasonably well. The Chinese and the Estonian samples stand out clearly in separate clusters compared to Gubbacka samples. The Salme nails from the boat grave are separated clearly from the Estonian contexts of Tuiu and Raatvere. The samples from Tuiu from Saaremaa are even separated slightly from Raatvere mainland sample. Furthermore, OMA iron samples are scattered all around the cluster plot – as they should due to different manufacturing processes. This all was very encouraging results and will be used in the future as well, though all was not roses for the elemental analyzes.

9. DISCUSSION AND OUTLOOK

If multiple samples from same artifact are run and the dates obtained are widely variable, iron is probably reworked and unsuitable for dating. Reworked material is often inhomogeneous with respect to the age of the carbon in the metal due to variations in absorption. If radiocarbon date does not match the date expected, it is possible to deduce something about the manufacturing process. (Cook et al. 2003b: 22.) When dating archaeological find materials, it is good to know the context where the artifacts originate and are found from. Typology can also operate as a guideline for dating results. As a curiosity, radiocarbon dating can also be used as a test method to reveal ancient items that are suspected to be latter-day forgeries.

We developed our pretreatment procedure to be based strongly on the techniques developed by Cook and Hüls. Because the risk of contamination is on its biggest during the milling of the sample, we decided to use aluminum oxide discs instead of metallic drilling or cutting tools. Hüls et al. (2011) are especially concerned that the contamination may derive from the modern steel tools that are used in the sample pretreatment. This is a serious risk and goes for cutting oil as well, which should not be used at all during the milling process. If the carbon content of the sample is mortally high, iron may sparkle and iron powder can take fire. This is a risk of contamination, because when the powder burns, it intakes carbon from the indoor air. Burnt iron should never be used as a sample material. To avoid a situation like this, it is good to mill the samples with a multitool, which revolution can be adjusted manually into lower the level.

Almost half of the samples (Hela-1997, Hela-1998, Hela-2149, Hela-2150, Hela-2520, Hela-2521, Hela-2530, Hela-2531) we analyzed indicate that the items have been smelted by using either coal, peat or limestone or the blacksmiths have used coke as a fuel in the forge. The risk is obvious and thus the elemental analyses should be conducted first. ICP-OES is probably the best technique to trace the elements from pulverized iron samples, but this kind of research should be realized in co-operation with the metallurgist, archaeologist, physicists and why not a blacksmith too. Preparing and the pretreatment of a single radiocarbon sample take over one week of laboratory work, so all wasted work should be avoided beforehand by investigating if the sample is

even suitable for the radiocarbon dating. If coke is used as a fuel in nearly every medieval forge, dating of iron might not be the best way to date the archaeological sites. If Aikarauta project continues, we should test longer time for combustion and use silver wool to remove impurities from the samples. Graphitization can be hindered by sulphur, thus the CO_2 should be purified twice or three times, if necessary. My opinion is that nails should not be dated at all, because these items are usually recycled, re-used and re-forged so many times, that use of coke in the forge and iron´s own age make it just absolutely impossible to get any reasonable dating results.

Still, we managed to test that our method fundamentally works. Our reference steels (RR-1 and RR-6) from Rautaruukki Company gave a result that was close to our background level 38000 BP. The reference iron cakes OMA-2, OMA-3 and OMA-4 gave dating results which were modern, as we supposed. The Estonian samples from Tuiu and Raatvere, Gubbacka and Gammelby irons gave also quite reasonable results, though systematic uncertainties of a few hundred years is probably explained by fossil contamination from the coke or re-use of iron. And as a cherry on a top – HelaH-38 sample actually gave almost a perfect match.

The dates were often systematically too old, not too young. This is in itself significant since typical problems in radiocarbon dating, like leakages in vacuum vessels induce too young samples but not too old. This fact, coupled to the fundamentally well-working technique as demonstrated by the modern and fossil samples, indicates that the systematically too old results are indeed due to some intrinsic challenges in the samples themselves and not by the method.

The research should be continued in co-operation with specialists from different the branches of science – internationally, of course. Particularly, to exploit the data from elemental analyses and to develop the methodology further, the Aikarauta project would require a person who would have expertise in metallurgy. The direct sputtering is a method which should be re-examined and work on. If the carbon could be sputtered off straight from the metal sample without time consuming pretreatment process, the research could be extended to investigate more valuable artefacts than nails and coins.

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With a great help of blacksmith Seppo Kallio, the Aikarauta project smelted four different batches of iron, which were produced with different flux types to test how flux would affect on radiocarbon dating results and what kind of differences are seen in elemental analyses and between $^{13}C/^{12}C$ stabile isotope ratios. Modern iron samples as a reference material were supplied by Rautaruukki Oyj. Elemental analyses were conducted by Alan Witick from the Institute for Environmental Research, University of Jyväskylä (ICP-OES-measurements) and Juhani Virkanen from the Department of Geosciences and Geography, University of Helsinki (ICP-MS-measurements). I got great help and wise advices with sample pretreatment from a senior laboratory technician, Anne-Maija Fors and the $\delta^{13}C$ values were measured by research engineer Igor Shevchuk, Dating Laboratory.

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APPENDICES

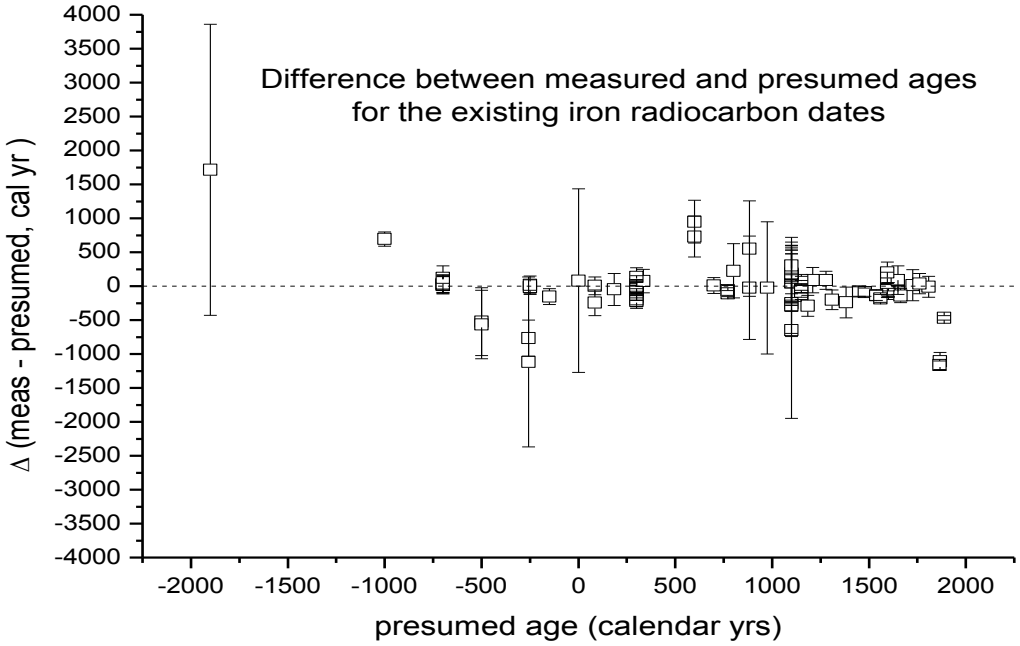

Figure I: 114 iron samples have been dated by ^{14}C-technique thus far.

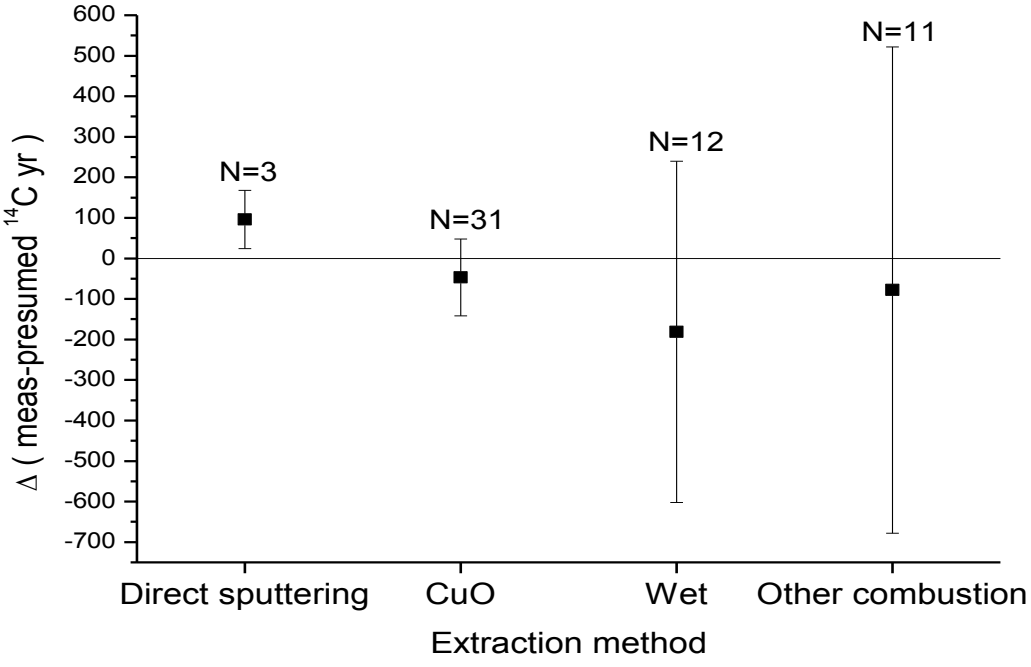

Figure II: Difference between measured and presumed ages for different carbon extraction methods.

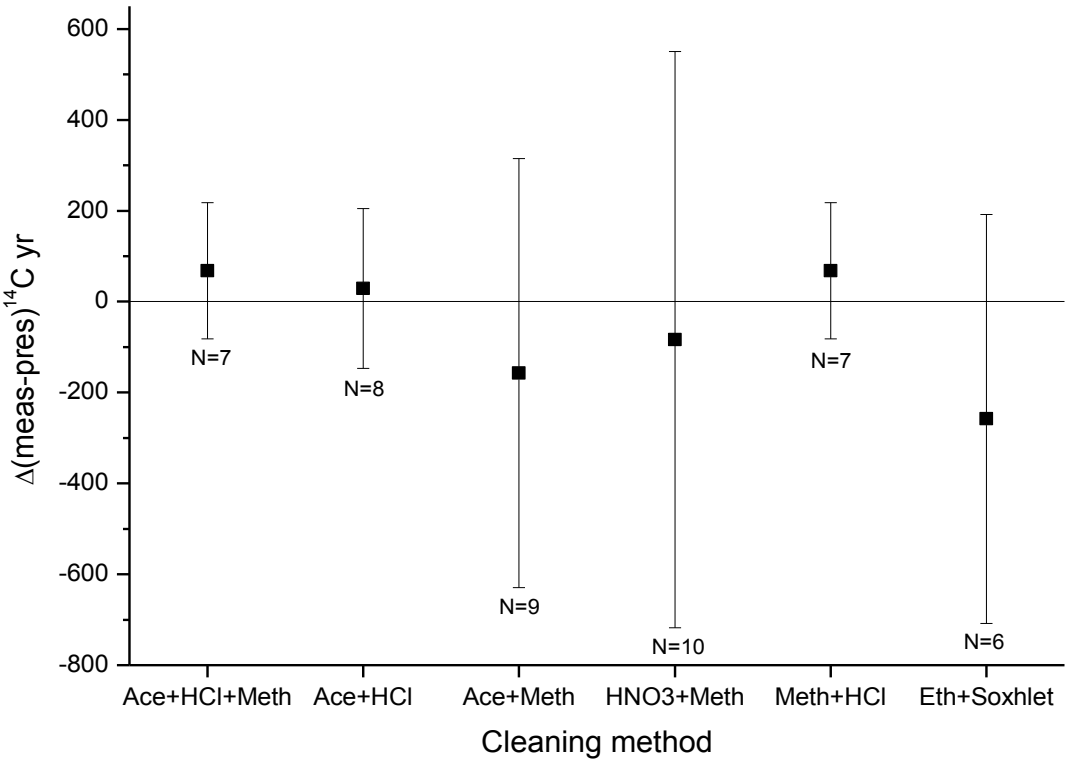

Figure III: Difference between measured and presumed ages for different sample cleaning methods. Mechanical cleaning was not counted as a variable because it was used in most cases.

Table I. All ^{14}C-datings of iron-based items (dated by AMS-method). The Aikarauta-samples are not listed here.

Artifact Identification	**^{14}C B.P.**	**%C**	**Presumed manufacture**	**Calibrated Date**
Damascus knife	240 ± 19	2,13	1650 A.D.	A.D. 1640–1670
Bloomery iron, Scotland	1930 ± 50	0,13	83–87 A.D.	B.C. 40–A.D. 220
Cast iron, Hopewell, PA	160 ± 40	4,08	1771–1845 A.D.	A.D. 1650–1950
Hook from Horyuji Temple, Japan	1330 ± 110	0,18	Late 7th–early 8th cent.	A.D. 604–814
Raw-Iron, Metzingen-Neuhausen 13856 c, Germany	885 ± 30		1100-1200 A.D.	A.D. 1060-1220
Sword, Nydam 18268 a-2, Germany	1755 ± 30		200-400 A.D.	A.D. 241-336
Nikko Shrine, large bracket	210 ± 50	0,13	1634-1636 A.D. 1818 A.D.	A.D. 1530-1950
Ingolstadt "Luppe" 16640 a, Germany	2185 ± 25		300-200 B.C.	B.C. 360-170
Milet Steel-Ball 13855 d, Germany	2575 ± 40		700 B.C.	B.C. 810-560
Ingolstadt "Luppe" 16640 b, Germany	2145 ± 25		300-200 B.C.	B.C. 350-110
Eylon's own sample B	1210 ± 140	.	180 or 1587 A.D.	A.D. 568–1151
Milet Steel-Ball 13855 c, Germany	2540 ± 35		700 B.C.	B.C. 795-557
Sword, Nydam 18268 1, Germany	1780 ± 25		200-400 A.D.	A.D. 220-330
Milet Steel-Ball No. 5, Germany	2555 ± 45		700 BC..	B.C. 810-540
Fishbourne nail, Sussex, U.K.	1070 ± 50	0,35	1–present A.D.	A.D. 890–1010
Sword, Nydam 18269 1, Edge, Germany	1705 ± 40		200-400 A.D.	A.D. 260-400
Cast iron, Redding Furnace, PA	160 ± 40	3,83	1761 A.D.	A.D. 1650–1950
Milet Steel-Ball 13855 b, Germany	2510 ± 75		700 B.C.	B.C. 791-530
Himeji Castle, small bracket	290 ± 50	0,12	1580-1610 A.D.	A.D. 1470-1800
Wrought-iron cleaver, Roman	1880 ± 40	0,38	27 B.C.-395 A.D.	A.D. 30-240
Sword, Nydam 18268 a-1, Germany	1785 ± 30		200-400 A.D.	A.D. 179-323
Himeji Castle, large nail	350 ± 40	0,01	1580-1610 A.D.	A.D. 1450-1640
Cast iron pin 3, Erl-5396, Sulzbach Castle, Germany	859 ± 87		8th-16th cent AD	A.D. 1020-1286
Denbigh, VA (N-20)	350 ± 40	0,41	17th cent. A.D.	A.D. 1440–1650
Cast iron pin 1, Erl-4247, Sulzbach Castle, Germany	842 ± 86		8th-16th cent AD	A.D. 1023-1290
Himeji Castle, pinch dog	390 ± 40	0,35	1580-1610 A.D.	A.D. 1430-1640
Iron nail 13854 b, Germany	1325 ± 35		732-811 A.D.	A.D 650-770
Raw-Iron, Metzingen-Neuhausen 13856 a, Germany	990 ± 25		1100-1200 A.D.	A.D. 1000-1160
Sword, Nydam 18268 d, Germany	1795 ± 25		200-400 A.D.	A.D. 138-318
Sword, Nydam 18269 b, Edge, Germany	1800 ± 25		200-400 A.D.	A.D. 136-318
Nail, earthquake fault in Turkey	1620 ± 50	0,55	250–420 A.D.	A.D. 260–560
Italian armor (N-7)	570 ± 50	0,66	Late 15th cent. A.D.	A.D. 1300–1440
Cast iron, Szechwan China	1770 ± 610	0,01	250 B.C–250 A.D.	B.C. 1250–A.D. 1410
Large spear, Burkina Faso, Africa	570 ± 30	0,3	1163-1393 A.D.	A.D. 1300-1430
Tie pin, Ipswich, MA (N-12)	230 ± 40	0,52	Late 17th cent. A.D.	A.D. 1530–1947
Small spear, Burkina Faso, Africa	740 ± 40	0,59	1042-1379 A.D.	A.D. 1220-1380
Italian armor plate (N-9)	510 ± 40	0,35	1480 A.D.	A.D. 1330–1450
Raw-Iron, Metzingen-Neuhausen 13856 d, Germany	810 ± 20		1100-1200 A.D.	A.D. 1220-1260
Iron nail 13854 a, Germany	1370 ± 35		732-811 A.D.	A.D. 644-683
Himeji castle nail, small	373 ± 31	0,28	1600 A.D.	A.D. 1440–1530
Milet Steel-Ball 13855 a, Germany	2425 ± 50		700 B.C.	B.C. 760-400

Cast iron pin averaged, Erl-5396, Germany	808 ± 48		8th-16th cent AD	A.D. 1156-1290
Japanese tanto tang	490 ± 40	0,44	1539 A.D.	A.D. 1330-1480
Sword, Nydam 18268 b-2, Germany	1640 ± 35		200-400 A.D.	A.D. 344-528
Cast iron, Saugus MA	420 ± 40	3,63	1648–1678 A.D.	A.D. 1420–1630
Cast iron, Erl-5532, Sulzbach Castle, Germany	754 ± 49		8th-16th cent AD	A.D. 1186-1302
Raw-Iron, Metzingen-Neuhausen 13856 b, Germany	1040 ± 25		1100-1200 A.D.	A.D. 990-1018
Sword-a 16638, Germany	2290 ± 75		200-100 B.C.	B.C. 410-200
Sword, Nydam 18268 b-1, Germany	1880 ± 20		200-400 A.D.	A.D. 79-207
Cast iron, Erl-6002, Sulzbach Castle, Germany	717 ± 49		8th-16th cent AD	A.D. 1218-1323
Cast iron pin 2, Erl-4248, Sulzbach Castle, Germany	740 ± 78		8th-16th cent AD	A.D. 1157-1401
Basque nail, Labrador coast, Canada	530 ± 70	0,10	Mid-1560s A.D.	A.D. 1320–1440
Galu, white cast iron (Africa)	740 ± 70	2,00	8th–16th cent. A.D.	A.D. 1170–1400
Sword, Nydam 18269 a, Edge, Germany	1895 ± 25		200-400 A.D.	A.D. 74-130
Cauldron, Java Sea wreck	930 ± 50	10,97	1215–1405 A.D.	A.D. 1000–1220
Himeji Castle, medium nail	180 ± 40	0,26	1580-1610 A.D.	A.D. 1640-1950
Sword, Nydam 18268 c, Germany	1905 ± 35		200-400 A.D.	A.D. 35-130
Sri Lankan wootz steel	980 ± 40	2,60	5th–13th cent. A.D.	A.D. 1012–1038
Japanese sword	880 ± 150	0,49	A.D. 1192–1573	A.D. 1021–1263
Wrought-iron nails, Roman	2090 ± 50	0,52	85 A.D.	B.C. 350-A.D. 30
Iron nail, Erl-5893, Sulzbach Castle, Germany	1158 ± 104		8th-16th cent AD	A.D. 660-1036
Ungwana, bloomery steel (Africa)	1210 ± 140	0,40	8th–16th cent. A.D.	A.D. 595–1030
Roman period arrowhead	1130 ± 50	0,11	1096-1272 A.D.	A.D. 770-1020
Ungwana, crucible steel (Africa)	530 ± 90	1,40	8th–16th cent. A.D.	A.D. 1290–1520
Frobisher bloom #3, 5 cm in	500 ± 60	0,20	1866–1911 A.D.	A.D. 1400–1442
MIT Luristan steel dagger	2880 ± 60	0,70	1st millennium B.C.	1012–1038 B.C.
Eylon's own sample A	473 ± 45		180 or 1587 A.D.	A.D. 1399–1474
ROM Luristan steel dagger	2940 ± 60	1,50	1st millennium B.C.	1137–992 B.C.
Ungwana, crucible steel (Africa)	1360 ± 650	0,30	8th–16th cent. A.D.	785 B.C.–A.D. 1685
Spear blade, Israel	2270 ± 50	0,4	1000 B.C.	B.C. 410-200
Frobisher bloom #3, 2 cm in	550 ± 60	0,20	4th–10th cent. A.D.	A.D. 1307–1355
Iron, Erl-5528, Staffelberg Mountain, Germany	1874 ± 48		500-15 BC	B.C. 1132-917
Cast iron, Hunan, China	340 ± 30	2,93	4th–10th cent. A.D.	A.D. 1450–1650
Galu, crucible steel (Africa)	1300 ± 70	1,70	1866 A.D.	A.D. 630–890
Staffelberg Soxhlet extraction	3103 ± 500		500-15 BC	B.C. 2602-148
Frobisher bloom #3, near surface	1340 ± 70	0,20	1845–1885 A.D.	A.D. 640–760
Gibson axe, Iraq	3740 ± 60	0,41	1900 B.C.	B.C. 2330-1960
Cahiague 26698, axe head	530 ± 80	0,14	Pre-19th cent. A.D.	A.D. 1385–1439
Anchor dedicated to Isonomae shrine	29520 ± 1300		Not avail.	NA
Modern steel, 1.3%C	39140 ± 970	1,30	Modern	NA
Modern steel, 1.9%C	38330 ± 2870	1,90	Modern	NA
Modern, coke-smelted cast iron	39800 ± 3000	3,28	Modern	NA
Modern bloom	>Modern	0,14	Modern, A.D. 1986	After A.D. 1950
Ball 2046: inner, axe head	>Modern	0,23	Pre-19th cent. A.D.	After A.D. 1950
Japanese folded steel	>Modern	0,55	1995 A.D.	After A.D. 1950
Himeji Castle, reforged nail	1890 ± 40	0,22	1580-1610 A.D.	NA
Nose ring, Burkina Faso, Africa	1830 ± 50	0,13	1292-1453 A.D.	NA

WWII steel, Fort SF	21890 ± 60	0,1	Early 1940s A.D.	NA
Roman iron, Colona Antonina, Italy	2200 ± 40	0,05	180-1587 A.D.	NA
Roman iron, Colona Antonina, Italy C	1470 ± 130	0,03	180-1587 A.D.	NA
Roman iron, Colona Antonina, Italy D	1980 ± 110	0,05	180-1587 A.D.	NA
Cast iron, Xian, China	Did not graphitize	0,03	221 B.C.– 220 A.D.	NA
Cahiague 26712b, axe head	1830 ± 70	0,04	Pre-19th cent. A.D.	A.D. 86–250
Planing adze, China	1720 ± 160	3,60	Late Han or Jin dynasty	A.D. 119–457
Cahiague 26712a, axe head, Ontario, Canada	1567 ± 137	0,04	Pre-19th cent. A.D.	A.D. 339–632
Cahiague 26697, axe head	1506 ± 410	0,06	Pre-19th cent. A.D.	A.D. 73–956
Galu, bloomery steel (Africa)	1400 ± 240	0,30	NA	A.D. 125–1050
Aromatic resin, Java Sea wreck	710 ± 70		NA	AD 1215-1405
Italian armor (N-5)	1640 ± 50	0,20	1400 A.D.	NA
Italian sword (N-8)	4250 ± 50	0,11	16th cent. A.D.	NA
German armor (N-6)	2790 ± 50	0,04	1550 A.D.	NA
German armor (N-11)	2580 ± 40	0,90	Mid-16th cent. A.D.	NA
Axle Thimble, Fort Lower Brule, SD (N-15)	13420 ± 110	3,55	1777–1778 A.D.	NA
Williamsburg, VA (N-21)	730 ± 40	0,18	1816–1817 A.D.	NA
Fort Atkinson, WI (N-18)	460 ± 40	0,04	1820–1827 A.D.	NA
Cast iron, Fort Berthold, ND	6610 ± 50	3,01	1845–1885 A.D.	6700 BP
Pail in Inari shrine	950 ± 100		1866 A.D.	NA
Cast iron, Fort Kiowa, SD	26390 ± 550	3,56	1870–1900 A.D.	NA
Gate from Myohouji Temple, Tokyo	38350 ± 2300	3,23	1866–1911 A.D.	NA
Ball 2046: outer, axe head, Ontario, Canada	3900 ± 180	0,11	Pre-19th cent. A.D.	2613–2137 B.C.
Iron nail, Erl-5544, Sulzbach Castle, Germany	5448 ± 60		NA	B.C. 4450-4050
Iron, Erl-5527, Staffelberg Mountain, Germany	5915 ± 69		NA	B.C. 4945-4600
Iron drill shavings, Erl-5530, Germany	15700 ± 140		NA	B.C. 17399-16138

Table II. Best dating results (<100 yr)

Artifact Identification	^{14}C B.P.	%C	Calibrated Date	Pre-treatment and extraction method
Damascus knife	240 ± 19	2,13	A.D. 1640–1670	Mech+HNO3+ace+eth+CuO
Bloomery iron, Scotland	1930 ± 50	0,13	B.C. 40–A.D. 220	CuO
Cast iron, Hopewell, PA	160 ± 40	4,08	A.D. 1650–1950	CuO
Hook from Horyuji Temple, Japan	1330 ± 110	0,18	A.D. 604–814	Mech+HNO3+meth+wet+other comb.
Raw-Iron, Metzingen-Neuhausen 13856 c	885 ± 30		A.D. 1060-1220	Mech+ace+CuO
Sword, Nydam 18268 a-2, Germany	1755 ± 30		A.D. 241-336	Mech+ace+CuO
Nikko Shrine, large bracket	210 ± 50	0,13	A.D. 1530-1950	NA
Ingolstadt "Luppe" 16640 a, Germany	2185 ± 25		B.C. 360-170	Mech+ace+CuO
Milet Steel-Ball 13855 d, Germany	2575 ± 40		B.C. 810-560	Mech+ace+CuO
Ingolstadt "Luppe" 16640 b, Germany	2145 ± 25		B.C. 350-110	Mech+ace+CuO
Eylon's own sample B	1210 ± 140	NA	A.D. 568–1151	NA
Milet Steel-Ball 13855 c, Germany	2540 ± 35		B.C. 795-557	Mech+ace+CuO
Sword, Nydam 18268 1, Germany	1780 ± 25		A.D. 220-330	Mech+ace+CuO
Milet Steel-Ball No. 5, Germany	2555 ± 45		B.C. 810-540	Mech+ace+CuO
Fishbourne nail, Sussex, U.K.	1070 ± 50	0,35	A.D. 890–1010	NA
Sword, Nydam 18269 1, Edge, Germany	1705 ± 40		A.D. 260-400	Mech+ace+CuO
Cast iron, Redding Furnace, PA	160 ± 40	3,83	A.D. 1650–1950	Mech+HNO3+meth+CuO
Milet Steel-Ball 13855 b, Germany	2510 ± 75		B.C. 791-530	Mech+ace+CuO
Himeji Castle, small bracket	290 ± 50	0,12	A.D. 1470-1800	NA
Wrought-iron cleaver, Roman	1880 ± 40	0,38	A.D. 30-240	NA
Sword, Nydam 18268 a-1, Germany	1785 ± 30		A.D. 179-323	Mech+ace+CuO
Himeji Castle, large nail	350 ± 40	0,01	A.D. 1450-1640	NA
Cast iron pin 3, Erl-5396, Germany	859 ± 87		A.D. 1020-1286	Wet+direct+meth+HCl+ace
Denbigh, VA (N-20)	350 ± 40	0,41	A.D. 1440–1650	Other comb.
Cast iron pin 1, Erl-4247, Germany	842 ± 86		A.D. 1023-1290	Wet+direct+meth +HCl+ace
Himeji Castle, pinch dog	390 ± 40	0,35	A.D. 1430-1640	NA
Iron nail 13854 b, Germany	1325 ± 35		A.D 650-770	Mech+ace+CuO
Raw-Iron, Metzingen-Neuhausen 13856 a	990 ± 25		A.D. 1000-1160	Mech+ace+CuO
Sword, Nydam 18268 d, Germany	1795 ± 25		A.D. 138-318	Mech+ace+CuO
Sword, Nydam 18269 b, Edge, Germany	1800 ± 25		A.D. 136-318	Mech+ace+CuO
Nail, earthquake fault in Turkey	1620 ± 50	0,55	A.D. 260–560	NA
Italian armor (N-7)	570 ± 50	0,66	A.D. 1300–1440	Other comb.
Cast iron, Szechwan China	1770 ± 610	0,01	B.C. 1250–A.D. 1410	Mech+HNO3+meth+direct+other comb.
Large spear, Burkina Faso, Africa	570 ± 30	0,3	A.D. 1300-1430	NA
Tie pin, Ipswich, MA (N-12)	230 ± 40	0,52	A.D. 1530–1947	NA
Small spear, Burkina Faso, Africa	740 ± 40	0,59	A.D. 1220-1380	NA
Italian armor plate (N-9)	510 ± 40	0,35	A.D. 1330–1450	HNO3
Raw-Iron, Metzingen-Neuhausen 13856 d	810 ± 20		A.D. 1220-1260	Mech+ace+CuO

NA= not available

Table III. Pre-treatment and carbon extraction methods in percentages for the best radiocarbon dating results (<100 yr).

Pre-treatment and extraction method	**%**
Mechanical cleaning+acetone+CuO	42
Mechanical cleaning+HNO3+acetone+ethanol+CuO	3
Mechanical cleaning+HNO3+methanol+wet method+other combustion	3
Mechanical cleaning+HNO3+methanol+CuO	3
Wet method+direct sputtering+methanol+HCl+acetone	5,3
Mechanical cleaning+HNO3+methanol+direct sputtering+other combustion	3
CuO (cleaning method unknown)	5,3
Other combustion (cleaning method unknown)	3
HNO3 (combustion method unknown)	3
NA (methods not available)	29
CuO combustion total	53
Other combustion total	11
Wet method total	8
Direct sputtering total	8